RESEARCH PROJECT NO. FHWA-MTDOH-7930

HIGH PRESSURE LIQUID CHROMATOGRAPHY AS A METHOD OF MEASURING ASPHALT COMPOSITION

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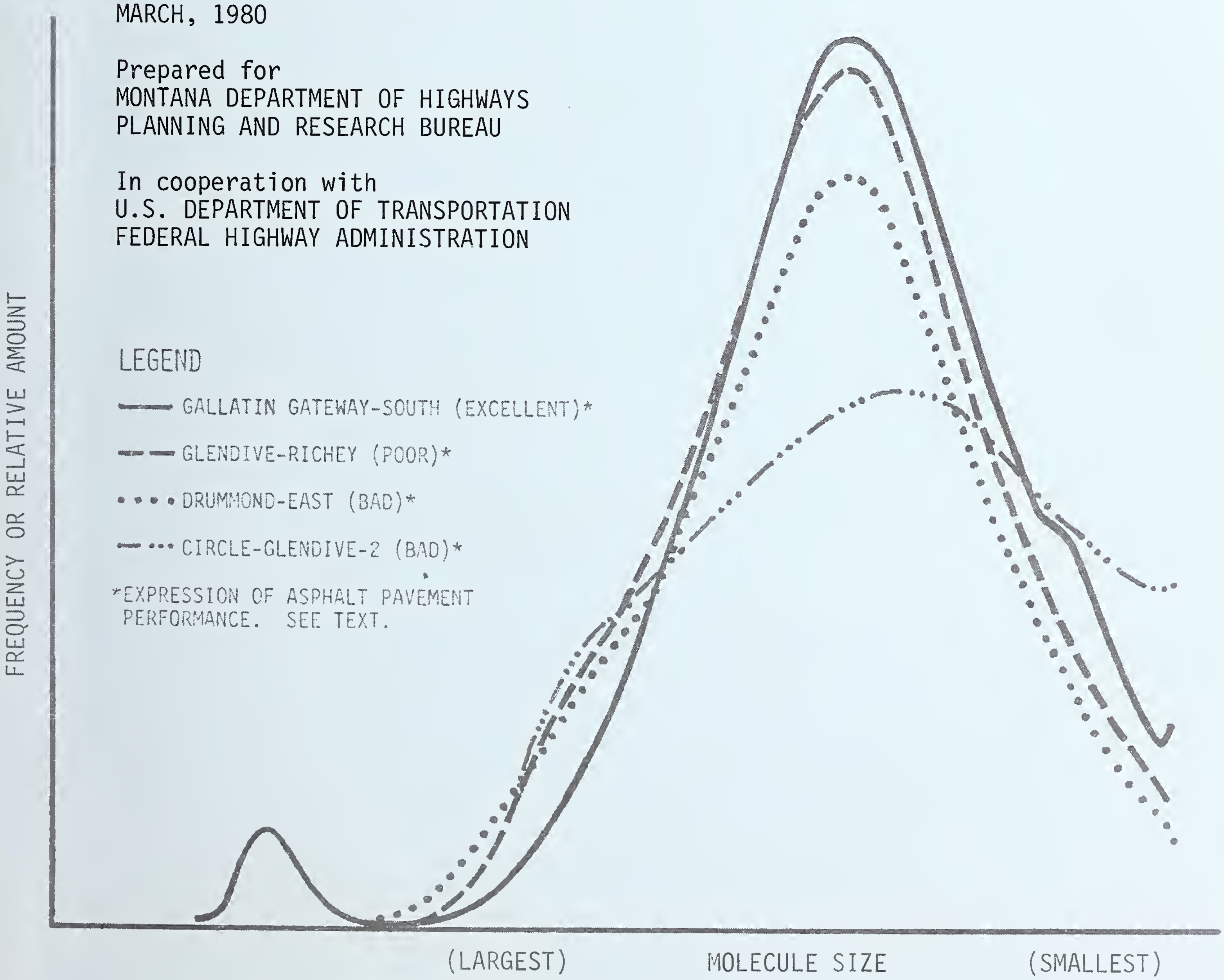
MARCH, 1980

Prepared for
MONTANA DEPARTMENT OF HIGHWAYS
PLANNING AND RESEARCH BUREAU

In cooperation with
U.S. DEPARTMENT OF TRANSPORTATION
FEDERAL HIGHWAY ADMINISTRATION



SIZE / FREQUENCY DISTRIBUTIONS OF ASPHALT MOLECULES (AS DETERMINED BY HPLC METHOD) BY HIGHWAY PROJECT

REPORT NO.

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Technical Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle	5. Report Date
High Pressure Liquid Chromatography as a Method of Measuring Asphalt Composition	March 1980
	6. Performing Organization Code
7. Author(s) Jennings, P. W., Pribanic, J., Campbell, W., Dawson, K., Shane, S., and Taylor, R.	8. Performing Organization Report No.
9. Performing Organization Name and Address Department of Chemistry Montana State University Bozeman, Montana 59717	10. Work Unit No. (TRAIS)
	11. Contract or Grant No. HPR-7930
12. Sponsoring Agency Name and Address Montana Department of Highways Helena, MT 59601	13. Type of Report and Period Covered Final Report
	14. Sponsoring Agency Code

15. Supplementary Notes

Prepared in cooperation with U.S. Department of Transportation, Federal Highway Administration.

16. Abstract

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HPLC has been used to characterize the asphalts produced by each of Montana's refineries. It has also been used to follow the changes in the molecular size distribution which result from mixing with aggregate and with lime. These results suggest that the molecular size characteristics of asphalt may be engineered to more closely approach the model. It is also suggested that HPLC analysis may be valuable in designing pavement recycling projects.

HPLC has been shown to be a more accurate measure of asphalt quality than asphaltenes content, penetration or ductility.

17. Key Words	18. Distribution Statement
asphalt, asphaltic/bituminous pavement cements, pavement durability/longevity, asphalt chemical composition/fractionation, high pressure liquid chromatography, molecular size frequency profiles, asphalt aging/deterioration, standard materials specifications, solvents/solubility/extraction methods, asphalt "finger printing", effects of pavement production plants, effects of oil refinery processing.	Unlimited availability

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	82	

Form DOT F 1700.7 (8-72)

Contents

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Abstract

The molecular size composition of asphalt as determined by high pressure liquid chromatography (HPLC) has been related to the performance of bituminous roadways in the state of Montana. HPLC and asphaltenes analyses have been used to define the characteristics of an asphalt which has shown satisfactory durability and longevity. These characteristics have been proposed as a model of high quality asphalt.

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INTRODUCTION

BACKGROUND

The ultimate success of an asphalt pavement depends on the interactions among a number of factors including subgrade and base course, aggregate, processing, additives, climatic conditions, etc., and, of course, the asphalt itself. The failure of any one of these factors can result in the early demise of the roadway.

Because these factors are so varied and the interactions so complex, it seems logical to attack one factor at a time. Indeed, many studies have been done on the asphalt cement alone. Some of these have resulted in specifications such as penetration and viscosity grading systems. Still others have searched for methods of quantifying the components of asphalt by solubility and/or reactivity (Corbett, 1969; Rostler, 1962).

Despite such studies, the assessment of asphalt cement quality remains a major concern. Such tests as ductility, penetration, viscosity, etc., employ physical parameters that measure only colligative properties and do not define the asphalt fully. For example, two asphalts of a given penetration grade used under similar conditions may or may not give similar performance on the roadway. Furthermore, viscosity graded asphalt meeting specifications for AC 10 could be penetration graded between 70 and 200+. Clearly, quality is not well controlled at present. One reason may be that such

tests do not totally reflect the chemical composition of the asphalt.

It would be ideal to separate each of the components of an asphalt and unravel the chemical and physical interactions of the various molecules. That is, of course, a formidable if not an impossible task. There are, however, methods for partial separation of components. Work by Rostler and Corbett was mentioned above. Another approach is through use of high pressure liquid chromatography (HPLC). Use of this tool has been the main subject of the research to be reported here.

SUMMARY OF FIRST PROJECT

Preliminary work on the use of HPLC as a tool in the study of asphalt quality was carried out in this laboratory (Jennings, 1977). Gel permeation columns, which separate components of a mixture by molecular size, were chosen. HPLC analyses were carried out on asphalt cements obtained from roadways which ranged in quality from good to bad. The result of these analyses was a series of chromatograms showing significant differences among the asphalts with regard to molecular size of components. In other words, HPLC provided a "fingerprint" of each asphalt. Coupling this information with certain physical tests and with knowledge of relative amounts of asphalt sub-fractions, a reasonable explanation for the performance of each of the roadways emerged. It appeared that HPLC could potentially be used not only to diagnose the reasons for failures of older roadways, but also to predict the performance of new asphalt roadways. It was

to further refine these possibilities that the current project was undertaken.

OBJECTIVES

In order to accomplish this refinement, a number of specific goals for the current project were established. This list of objectives will form the outline of the discussion section to follow.

I. Establish workable procedures for the preparation of asphalt for analysis.

II. Refine the procedures for HPLC analysis and for interpreting the resulting chromatograms.

III. Investigate refinery processing.

IV. Conduct a broader study of established roadways.

V. Study the changes in asphalt due to mixing with aggregate, fly ash or lime using 1978 roads.

VI. Estimate the effects of aging.

VII. Characterize a model of excellent asphalt.

VIII. Apply the model to predict the performance of 1978 and 1979 asphalts.

IX. Investigate application of HPLC technique to other areas, e.g., the Wibaux recycling project.

Results and Discussion

I. ESTABLISH WORKABLE PROCEDURES FOR THE PREPARATION OF ASPHALT FOR ANALYSIS.

A key consideration in preparing asphalt for analysis by HPLC was to maintain the asphalt in its "natural" state as much as possible. Therefore, techniques which employ extreme heat or induce needless chemical reactions (e.g., use of acids) were avoided.

A. *Comparison of procedures and of solvents for extraction of asphalt from aggregate.*

During the first project, asphalt was extracted from pavement cores using tetrahydrofuran (THF) in a Soxhlet extractor. Due to the nature of the Soxhlet extraction process, this procedure required 1 to 3 weeks to remove all the asphalt from aggregate. The time element proved to be unsatisfactory.

Although THF is an excellent solvent for asphalt, it was shown in the current study to react with lime which is a frequent component of paving mixtures. Benzene and trichloroethylene (TCE), while not dissolving asphalt quite as rapidly as THF, are both suitable solvents. and are prescribed by AASHTO. Both benzene and TCE were shown to remove asphalt completely from aggregate. Neither solvent appeared to cause extraneous reactions with asphalt. They were shown not to react with lime. Benzene was selected in the last analysis because

it is less expensive than TCE.

Three extraction techniques were tested. Ultrasonification, reflux and vacuum extraction methods (AASHTO designation: T 164-76), were all found to remove asphalt from aggregate satisfactorily. However, the reflux method is more rapid (about 12-24 hours), and requires less technician time than either of the other methods. Reflux equipment is not too expensive. Therefore, reflux was the extraction method of choice.

B. *Comparison of procedures for removal of solvent from extracted asphalt.*

During the first project, a Büchi rotary evaporator (rotovap) was used to remove the bulk of the solvent from the extracted asphalt. Final traces of solvent were removed by placing the asphalt in a vacuum oven at 80° for 8 hour periods until constant weight was obtained (Jennings, 1977).

Two other methods of solvent removal were compared to the above vacuum oven technique: the rotovap alone and the Abson method.

The Abson method (AASHTO designation: T-170) involves removal of solvent at 160-166°C while bubbling CO_2 through the solution. This is a very slow process when large amounts of solution are involved, so it was modified slightly in that the bulk of solvent was removed by rotovap and final traces by Abson method.

In the rotovap method, solvent was removed in two stages. First, the bulk of the solvent was removed by the rotovap. Second, after

transfer of the asphalt and remaining solvent to a smaller container, final traces of solvent were removed by operating the rotovap at 128-130°C at a reduced pressure of 24-26 mm Hg for 20 minutes.

The rotovap method was considerably faster than the use of vacuum oven and somewhat faster than the modified Abson. It required less technician time than either method and was easier to control.

To ascertain that no light-end material was being removed by the rotovap, a weighed sample of deasphalted gas oil (DAGO) was mixed with benzene and subjected to more vigorous roto-evaporation at 130-134°C and 17mm Hg for 45 minutes to remove benzene. Less than 0.1 percent of the oil was lost. Furthermore, no change was visible between HPLCs of original DAGO and DAGO after solvent removal.

Using this information it was decided that the rotovap would be used for solvent removal in this project.

C. *Comparison of procedures for subfractionation of asphalts.*

During the first project, a modification of the Corbett-Swarbrick method of asphalt fractionation was designed (Jennings, 1977; Corbett, 1969). Four fractions were obtained by this procedure; asphaltenes, light aromatics, heavy aromatics and saturates (paraffins). These fractionations were valuable in understanding the chromatograms of whole asphalts. The advantage of this technique is that conditions are mild and do not lead to chemical changes in the asphalt. Furthermore, the fractions are compatible with the columns and solvents used in HPLC analysis.

The Rostler-Sternberg fractionation method (Rostler, 1962) is a commonly used procedure and has been conducted in this laboratory. Two facts dictated that the method could not be used in this study: first, chemical treatment of the asphalt was so drastic that the asphalt could not be reconstituted to its original condition; second, the presence of strong acid in the fractions was not compatible with the columns and solvents used for HPLC.

Earlier work in this laboratory indicated that the percentage of asphaltenes [that fraction of asphalt which is insoluble in heptane (or hexane in the Rostler procedure)], is of major importance in the performance of an asphalt. Rostler's work also indicated this. As the current project progressed, it became evident that sufficient data for the purposes of the study would be provided by HPLC analysis of the whole asphalts and knowledge of the percentage of asphaltenes present in each asphalt. Therefore, only the asphaltenes, or heptane-insoluble fraction of asphalt was isolated, using the Corbett procedure.

II. REFINEMENT OF HPLC PROCEDURES AND INTERPRETATION OF THE RESULTING CHROMATOGRAMS.

A. *Internal Standard*

A problem in the previous work arose when comparing chromatograms. Elution time (the time required for molecules of a given molecular size to traverse the system) is a function of a variety of parameters which tend to change from run to run. This is typical of all chromatographic techniques. Because of this fact, it was sometimes difficult

to make judgements about the sizes of molecules contained in different samples. This problem has been negated by use of an internal standard. Polystyrene, with molecules of known size, is injected with each sample. It forms a marker on the chromatogram (figure 1). Superimposing markers permits accurate comparison between chromatograms.

In order to have adequate separation between the internal standard peak and the asphalt chromatogram, two columns (10^5 Å and 10^6 Å) were added to the bank of columns used during the first project (three 500 Å and one 1000 Å).

B. Interpretation of HPLC Chromatograms

The HPLC system used in this study permits the largest molecules to pass most quickly through the columns but successively retards the progress of smaller molecules. This is reflected in the chromatograms shown in figure 1. The elution time is recorded in minutes along the ordinate. Large molecular size (LMS) materials elute in the shortest time and appear on the left of the chromatograms. (The small peak at the far left of the chromatograms represents the internal standard).

The chromatograms in figure 1 are compared by superimposing the internal standard peaks. As exemplified by this figure, chromatograms may differ in one or more of the following features:

1) Elution time of the largest molecules.

Of the two asphalts, "B" (dashed line) contains the largest molecules because they begin to elute earlier than large molecules of "A".

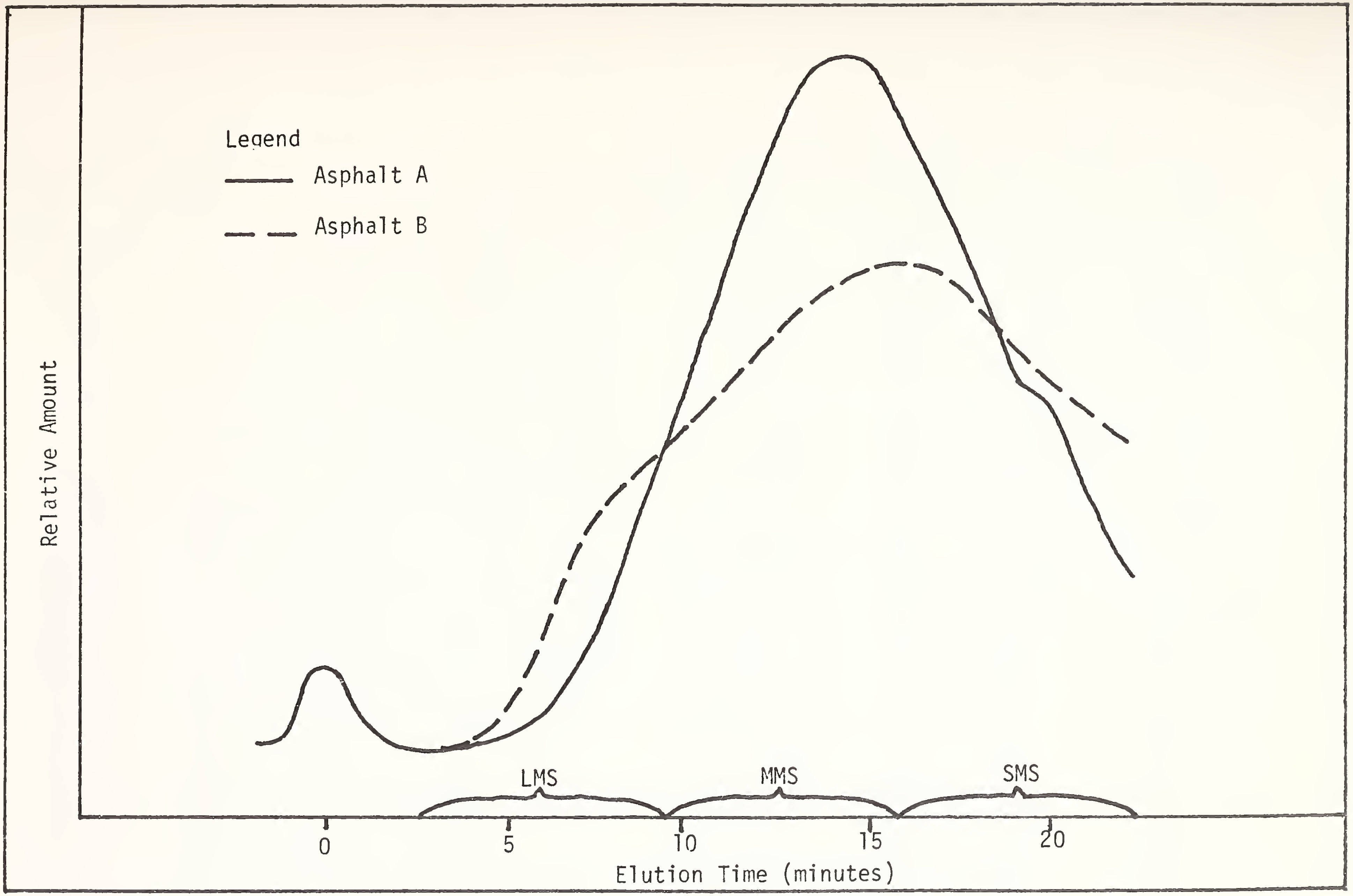

Figure 1. Typical chromatograms of whole asphalts

2) Height of the curve in the LMS region.

Asphalt "B" contains more LMS materials than "A". This is shown by the fact that height of the curve at a specific elution time in the LMS region is higher for "B" than for "A".

3) Elution time of the curve maximum.

The curve maximum for asphalt "A" occurred 14.5 minutes after elution of the internal standard peak. Asphalt "B" required 16 minutes. This means that the most numerous molecules in "B" are smaller than those in "A".

4) Height of curve maximum relative to height in LMS and SMS regions.

Asphalt "B" contains a much higher proportion of LMS and SMS (small molecular size) components to MMS (medium molecular size) materials than asphalt "A".

5) Height of the curve in the SMS region.

Asphalt "A" contains fewer SMS components than asphalt "B".

These features are listed above not only in order of their appearance on the chromatogram, but also in order of their importance to asphalt quality. It will be shown in Section IV.C. that the greater the disparities between the HPLC of a given asphalt and that of a standard asphalt of excellent quality, the poorer the performance of that asphalt. This is especially true with respect to the size and amount of LMS material. It should be pointed out that asphalt "B" is from a bad road and "A" is from an excellent road.

C. The contribution of asphaltenes to the HPLC chromatogram.

In the first project, the LMS region was ascribed entirely to

asphaltenes. This is not completely true.

The contributions of the asphaltenes (heptane-insoluble) and heptane-soluble fractions of asphalt to the LMS region is shown in figure 2. The dotted line on the chromatogram indicates the distribution of the asphaltenes fraction. The distribution of the heptane-soluble portion is shown by the dashed line. It is important to note that, although the asphaltenes fraction does account for most of the LMS components, soluble materials may also contribute large molecules. Furthermore, the asphaltenes fraction is not confined to very large molecular size components. It will be shown in later sections that both the amount of LMS material and the percentage of asphaltenes are very important in the determination of asphalt quality.

III. REFINERY PROCESSING

Each of the four Montana refineries was visited to study the processes by which asphalt is produced on the supposition that processing differences could contribute to observed differences in asphalt. The recurrent theme, however, had less to do with flow charts than with feed stocks. While refineries in the past processed fairly uniform crude oils into more-or-less predictable asphalts, crude stocks are no longer uniform. For example, crude oils from Wyoming's Elk Basin and from certain Montana sources yield about 30 percent asphalt, while Canadian crudes yield only 8 percent. All refineries appear to be mixing their feed stocks from available supplies. At one refinery, the crude supply was not controlled locally. In consequence, the

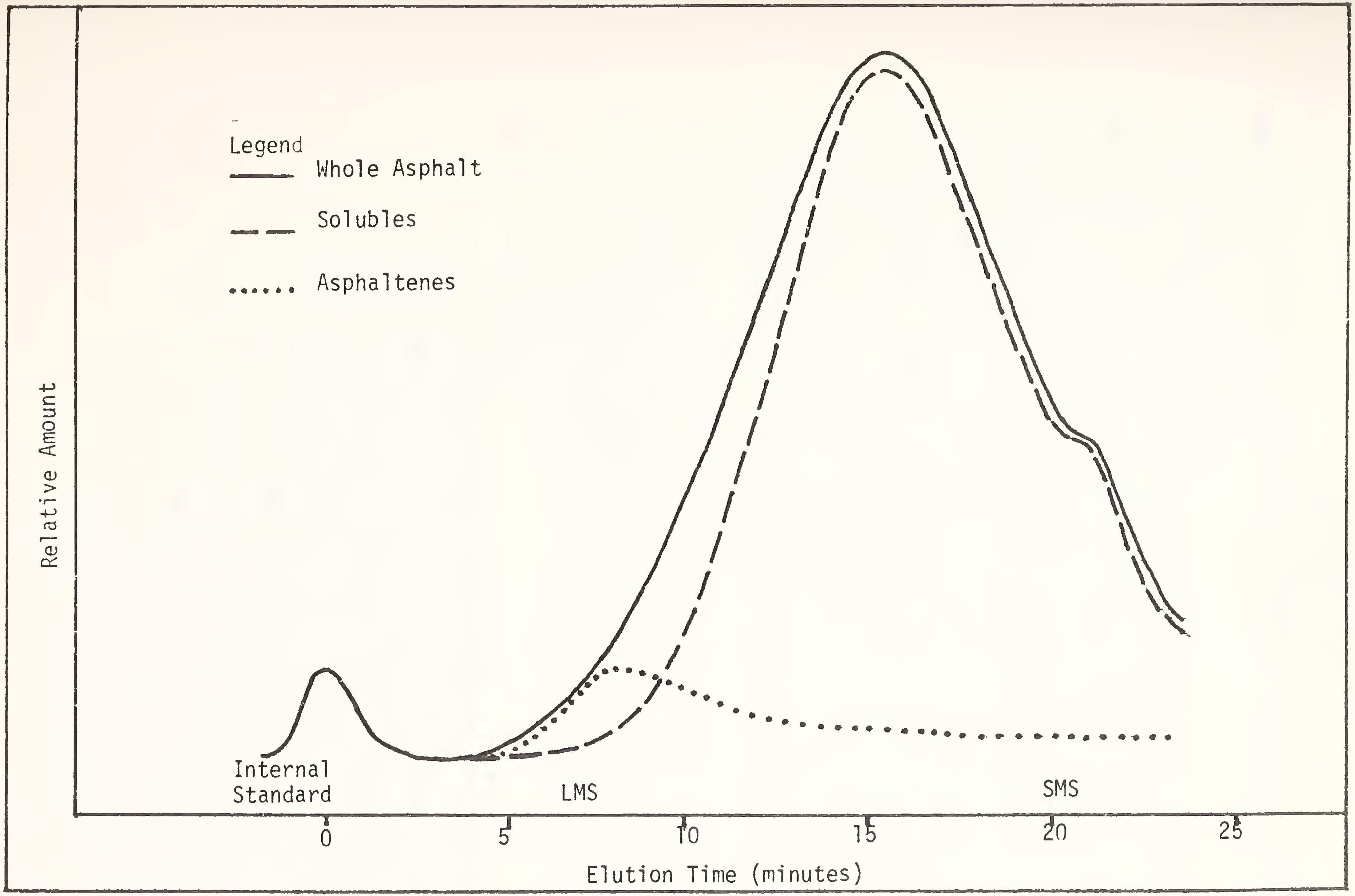

Figure 2. Molecular size distribution in asphalt

composition of present asphalt is a function of crude sources and may vary from refinery to refinery.

This is not to minimize the effects of processing, although these effects may be more easily observable on older roadways. In Table 1 are outlined only those steps in the refining process which lead to asphalt production for each of the Montana refineries.

In phases I and II, processes at the four refineries are not vastly different. However, an estimate of their potential differences may be made. If it is assumed that all refineries are using the same feed stock and are operating at the divergent extremes of their ranges of conditions, the relative rigor of the processes may be estimated:

Refinery D > C > A > B

This means that, assuming these extreme conditions, the penetration of asphalt at the end of Phase II at each refinery would be expected to increase in the same order, that is, Refinery B would produce softer asphalt than Refinery D.

Refineries A, C and D produce asphalt directly from the vacuum distillation unit (Phase II). Refinery C stated that the pen grade of its asphalt was controlled by adjusting crude mixture and/or temperature and pressure in the vacuum unit. Refinery D reported only that it's asphalt was stored in lots by pen grade (85-100, 120-150, 200-300). Refinery A reported that the asphalt from its vacuum unit ran between 80 and 120 pen. Refinery B also produced asphalt from its vacuum unit, but this was 500 pen material used only for blending.

Table 1

REFINERY PROCESSES

Refinery	A	B	C	D
Crude Source	mixed	mixed (≈ 15% asphalt)	mixed	mixed (~ 18% asphalt)
Phase I - Crude Fractionation	730° F 20-30 psi	700° F 30 psi	650-700° F 1 atm	330° F 13 psi ↓ 720° F 6 psi
Phase II - Vacuum Distillation	730-750° F 50mm Hg	710-760° F 60-70mm Hg	800° F 30mm Hg	700-800° F 20mm Hg
Phase III - (Finishing)	→ Asphalt 80-120 → PDA unit → gas oil → pitch	→ Asphalt 500 pen → PDA unit 150-170° F 450 psi → DAGO → asphalt 60-70 or 85-100	Asphalt → * → fluid coker → coke *pen controlled by crude and Phase III	Asphalt stored as 85-100 120-150 200-300 pen

There are notable differences in Phase III processes. Both refineries A and B use a propane deasphalting (PDA) process (a co-distillation with propane in which lower-boiling gas oil is removed from the asphaltic material). However, only part of the asphaltic material from the vacuum tower is routed through the PDA unit in refinery A. There the products of the PDA unit are gas oil and pitch, a very hard asphaltic material. The pitch is apparently not returned to the asphalt. At refinery B, all of the asphaltic material from the vacuum tower (except for the 500 pen asphalt mentioned earlier) is routed through the PDA unit. In this case, the products of the PDA unit are asphalt and deasphalted gas oil (DAGO).

At refinery C, excess asphalt can be run through a fluid coking unit to produce coke for which other outlets are available.

Refinery A blends higher penetration asphalts from its basic 80-120 stock. Refinery B blends pen graded asphalts from its 60-70 or 85-100 stock with 500 pen material and with DAGO. Refinery C, as stated previously, controls asphalt grade at the vacuum tower. Refinery D reportedly blends asphalts, depending on inventory.

Asphalt resulting from the PDA process has a higher percentage of LMS materials than asphalt from other processes. This could be of considerable benefit in asphalts derived from Canadian crudes because they are deficient in LMS materials.

It is also possible that "taking the asphalt apart", so to speak (i.e., removing gas oil) and then reconstituting it by blending the gas

oil back into the harder asphalt enables meeting pen grade specifications but has somehow compromised the integrity of the asphalt.

Based on these observations and others to come later in this report, refineries A and B currently produce asphalts which contain relatively small amounts of LMS materials; asphalt from refinery C contains somewhat larger amounts of LMS; refinery D produces asphalt with a still higher proportion of LMS components. The differences in the asphalts available could be a tremendous advantage to the Montana Department of Highways. That is, asphalts could be selected based on the needs of a given situation.

IV. A BROADER STUDY OF ESTABLISHED ROADWAYS

In the first project, a few established roads were investigated to briefly examine the feasibility of analyzing asphalt by HPLC. In this study, more roads from a wider range of design penetrations were investigated.

Established roadways have been studied in order to find the characteristics of the more successful asphalts and to find the ways in which less successful asphalts differ in these characteristics. This study has been approached by:

1. Establishing criteria for the selection of samples;
2. Setting standards for rating the quality of roadways;
3. Obtaining HPLC information for the samples and interpreting the chromatographic data;
4. Studying the role of asphaltenes in asphalt quality;

5. Correlating the penetration and ductility of asphalt at sampling time with roadway performance, original design penetration and refinery source.

In this section, each of these points will be discussed in turn.

A. *Criteria for sample selection.*

Established roadways were selected for sampling by using the following criteria:

1. Obtain samples from asphaltic roadways in each of the design penetration classes (85-100, 100-120, 120-150, 150-200, 200-300).
2. Within each penetration class, obtain samples representing each of the four Montana refineries.
3. Within each penetration class, obtain samples from roadways of various ages.
4. Within each penetration class, obtain samples from roadways of various qualities, e.g., bad, poor, good and excellent.

Samples from a total of 39 established roadways were obtained by coring. Three cores were taken from each roadway from the right tire lane within a 1/4 mile section. Table 2 contains a list of these roadways along with other pertinent data.

B. *Standards for quality rating.*

Rating the quality of a roadway depended upon subjective judgement made upon direct observation. However, every effort was made to eliminate from consideration any roadway in which mat failure might have been related to factors other than the asphalt, such as

Table 2 Established Roadways

Identification	Age at Sampling (years)	Condition	Pen[a] 77°F	Ductility cm. 40°F	Filler	Plant Type	Refiner	Percent Asphaltenes[j]
85-100 Design Penetration								
1. Big Timber-Harlowtown F 45(12)U1	9	Bad (cracked after 2 yrs.)	49	5.5	1.5% lime	Pioneer C. F.[h]	B	16.2 (+0.7)
2. Terry-Fallon I 94-5(10)174	10	Bad TC, LC+++[d,e]	44	10.25	limestone dust	Barber-Greene C.F.	B	16.8 (+2.8)
3. Toluca-East I 90-9(30)483	9	Bad TC+++	58	6.0	?[m]	?	B	18.1 (+4.9)
100-120 Design Penetration								
4. Alzada-Ekalaka-1 S 318(4)	15	Bad-AC[k] TC, LC+++	38	1.5	-[n]	Batch	B	21.0 (-1.1)
5. Circle-Glendive-1 F 246(13)	15	Poor TC+++	44	2.0	mineral filler	Batch	B	20.0 (-4.0)
6. Terry-Brockway S 302(19)	13	Good TC++[f]	49	6.25	mineral filler	Pioneer C.F.	C	13.7 (-0.4)
7. 27th Street to Highway 87 I-IG 90-8(23)447 U2	13	Bad AC, TC, +++	28	0.5	limestone dust	C.F.	B	22.9 (+3.0)
8. Twodot-South S 18(6)	14	Excellent	62	9.0	-	Pioneer C.F.	C	17.9 (-2.1)
9. Wibaux-E & W[g] I 94-7(4)233 U1	15	Bad[g]	51	15	-	Cedar Rapids Batch	C	19.2 (+0.7)

a-Penetration of recovered asphalt
b-TC-Transverse Cracks
c-+ some cracking
d-LC-Longitudinal Cracks
e-+++-extensive cracking
f-++-moderate cracking
g-aggregate failure; asphalt recycled
h-C.F.=continuous flow plant
j-( )=difference between total asphaltenes & solubles recovered and 100%
k-AC-Alligator Cracking
m-?-unknown
n-not present

Table 2 (continued)

Identification	Age at Sampling (years)	Condition	Pen 77°F	Ductility cm. 40°F	Filler	Plant Type	Refiner	Percent Asphaltenes
120-150 Design Penetration								
10. Alzada-Ekalaka-2 S 347(14)	9	Good TC+	-	-	Hydrated lime	Cedar Rapids Batch	C	13.4 (+5.7)
11. Circle-Glendive-3 F 246(21)	3	Poor TC++	-	-	-	Batch	B	-
12. Crow Agency-Broadus F 334(18)	10	Good TC+	111	-	-	Batch	C	17.1 (+1.4)
13. Crow Agency-Hardin I 90-9(31)489	8	Good	138	70.5	fly ash	Barber-Greene C.F.	C	11.9 (-4.5)
14. Dawson Co. Line-East I 94-6(21)191 U1	6	Good TC++	92	42.5	fly ash	Batch	B	15.5 (+0.2)
15. Divide-North I 15-2(34)103 U3	3	Good TC+	62	4.5	?	Batch	B	12.5 (+1.6)
16. Judith Gap-East-1 S 174(5)	10	Good	68	9.5	Hydrated lime	Pioneer C.F.	C	16.3 (+0.4)
17. Judith Gap-East-2 S 174(4)	10	Good TC+	103	55.25	Hydrated lime	Cedar Rapids Batch	A	17.6 (+3.1)
18. March-Glendive S 359(11)	8	Good TC++	90	30	-	C.F.	B	15.3 (+3.2)
19. Musselshell River-E & W F-RF 256(36)U1	6	Good	105	68.5	fly ash	Barber-Greene Batch	C	13.0 (-3.2)
20. Prairie Co.Line-East I 94-5(11)166 U4	8	Bad, AC++ TC++	72	15	-	Standard Batch	B	12.1 (-3.7)
21. Rosebud-South S 252(3) U1	8	Good TC+,AC+	57	8.25	-	Cedar Rapids C.F.	B	14.4 (+1.2)
22. Wolf Point-Hungry Creek S 429(3)	10	Bad TC++	35	4.0	Hydrated lime	Cedar Rapids 6-60	F	22.9 (+1.5)

Table 2 (continued)

Identification	Age at Sampling (years)	Condition	Pen 77°F	Ductility cm. 40° F	Filler	Plant Type	Refiner	Percent Asphaltenes
150-200 Design Penetration								
23. Billings-South S 132(3)	19	Poor TC+, AC+	22	0.25	-	?	B	23.8 (-3.8)
24. Chester-Gildford F 132(7)	15	Bad AC, TC+++	70	12.0	-	Madsen Batch	F	21.6 (-1.8)
25. Circle-Glendive-2 F 246(9)	18	Bad TC, AC+++	65	3.25	-	Cedar Rapids Batch	B	23.3 (+0.5)
26. Drummond-East I 90-3(3)157 U1	19	Bad TC, AC+++	34	3.5	-	?	A	17.4 (-1.1)
27. Gallatin Gateway-Bozeman F 203(7)	19	Excellent	120	52.5	?	Pioneer C.F.	C	15.6 (+0.3)
28. Gallatin Gateway-South F 76(6)	19	Excellent	113	45.75	?	Pioneer C.F.	C	13.3 (-3.9)
29. Glendive-Richey S 32(9)	20	Poor TC, LC++	58	8.0	-	C.F.	G	14.1 (+0.3)
30. Hardy Creek-Cascade Old I 15-5(13)239 U1	16	Bad TC, AC+++	75	8.5	-	Standard Batch	D	22.2 (-0.5)
200-300 Design Penetration								
31. Brandenberg-Garland RS 45(14)	4	Good	210	100+	fly ash	Boeing Drum	C	13.8 (+1.1)
32. Busby-Lame Deer-1 RF-FLH 334(21)U1	5	Good TC+, rutting	191	-	-	Pioneer C.F.	B	14.4 (+2.9)
33. Busby-Lame Deer-2 RF-FLH 334(24)	4	Good	-	-	-	Stansteel	C	9.5 (+0.5)
34. Busby-Lame Deer-3 RF-FLH 334(25)	3	Good	209	-	-	Stansteel	B	15.6 (+1.2)

Table 2 (continued)

	Identification	Age at Sampling (years)	Condition	Pen 77°F	Ductility cm. 40°F	Filler	Plant Type	Refiner	Percent Asphaltenes
35.	Columbus-Rapelje RS 129(14)	3	Good	94	21.5	fly ash	Cedar Rapids Batch	A	18.7 (+5.4)
36.	Havre-Simpson S 301(17)	6	Good TC+, Deformation	111	21.5	fly ash	Pioneer C.F.	D	14.6 (-3.1)
37.	Thompson Falls-West F 7-1(1)	4	Good	200	75.5	-	Cedar Rapids Batch	D	12.9 (-2.7)

sub-grade problems, lack of voids, design errors,* etc. An "excellent" rating was reserved for those roadways more than 14 yearsold which exhibited very little, if any, cracking. Mats which contained few cracks between regular but widely spaced transverse cracks or which exhibited very little cracking but were less than 14 yearsold were classified as "good". Mats which exhibited more extensive cracking or which were beginning to crack at an early age (<10 years) were classed "poor". Only those roadways which were severely cracked, especially those showing extensive alligator cracking in addition to very frequent transverse and/or longitudinal cracks were classified as "bad".

C. *Interpretation of chromatograms of established roads.*

The established roadways listed in Table 2 were studied by HPLC. The chromatograms were first compared within design penetration classes. For example, the chromatograms of asphalt from four roads in the 150-200 penetration group are shown in Figure 3. Some pertinent data for these roads are condensed in Table 3.

Table 3

Road	Age	Condition	%Asphaltenes	Symbol
Gallatin Gateway-South	19	Excellent	13.3	________
Glendive-Richey	20	Poor	14.1	--------
Drummond-East	19	Bad	17.4	....
Circle-Glendive-2	18	Bad	23.3	-.-.-.-.

*Rutting is frequently thought to be related to the latter two problems. Furthermore, rutted roads were not observed when selecting roads for sampling and, therefore, no correlation could be made between rutting and HPLC profile. It may be that some recent asphalts which are very soft (i.e., contain small amounts of LMS components) will be subject to deformation and these should be studied in future work.

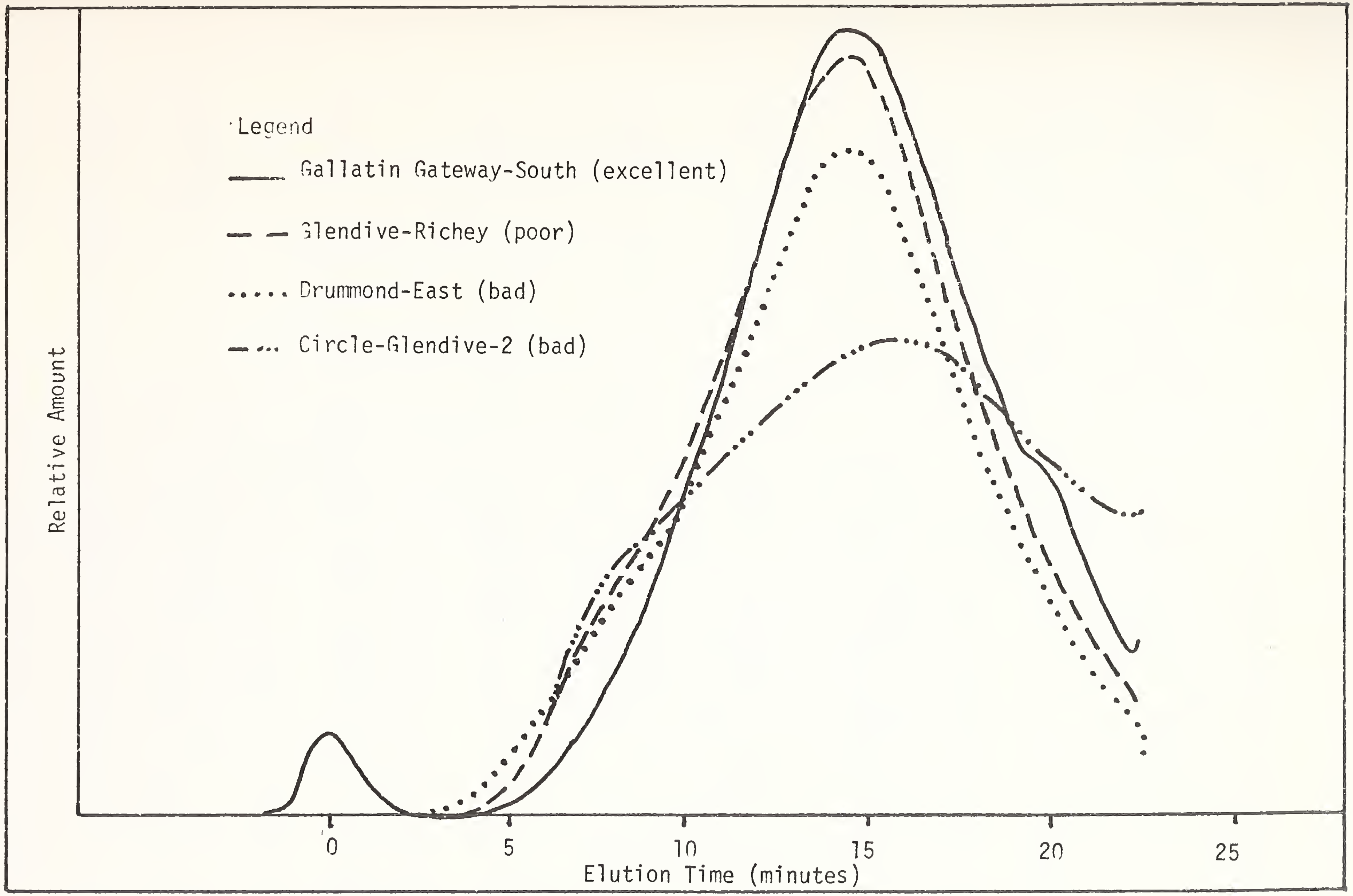

Figure 3. Established roadways, 150-200 design penetration.

Glendive-Richey, a "poor" road, differs from Gallatin Gateway-South ("excellent") primarily in the size and amount of the LMS components and in the size of the SMS materials. Drummond-East, classified as "bad", shows even greater differences especially in the LMS region. Circle-Glendive-2, another "bad" road, shows virtually no similarity to Gallatin Gateway-South.

Similar patterns emerge in other design penetration classes. In figure 4, the asphalts from two 85-100 class roads are compared to Gallatin Gateway-South, which was used for comparison because no excellent roads were available in this class. The 100-120 pavements are compared to Twodot-South, an "excellent" roadway (figure 5).

Gallatin Gateway-South is included in the comparison of 120-150 roadways (figure 6) because the oldest road sampled was only 10 years of age, not old enough to be rated "excellent". It is noteworthy that the chromatogram of Crow Agency-Hardin asphalt is nearly identical to that of Gallatin Gateway-South. The Crow Agency-Hardin road is good, but only 8 years old.

The 200-300 design penetration asphalts were also compared to Gallatin Gateway-South because the roads sampled in this class were no more than 6 years old (figure 7).

The validity of using Gallatin Gateway-South as a standard in these comparisons is born out by the data shown in figure 8. The chromatograms of the best available roadways in the 100-120, 120-150 and 150-200 design penetration classes are compared. It can be seen that the

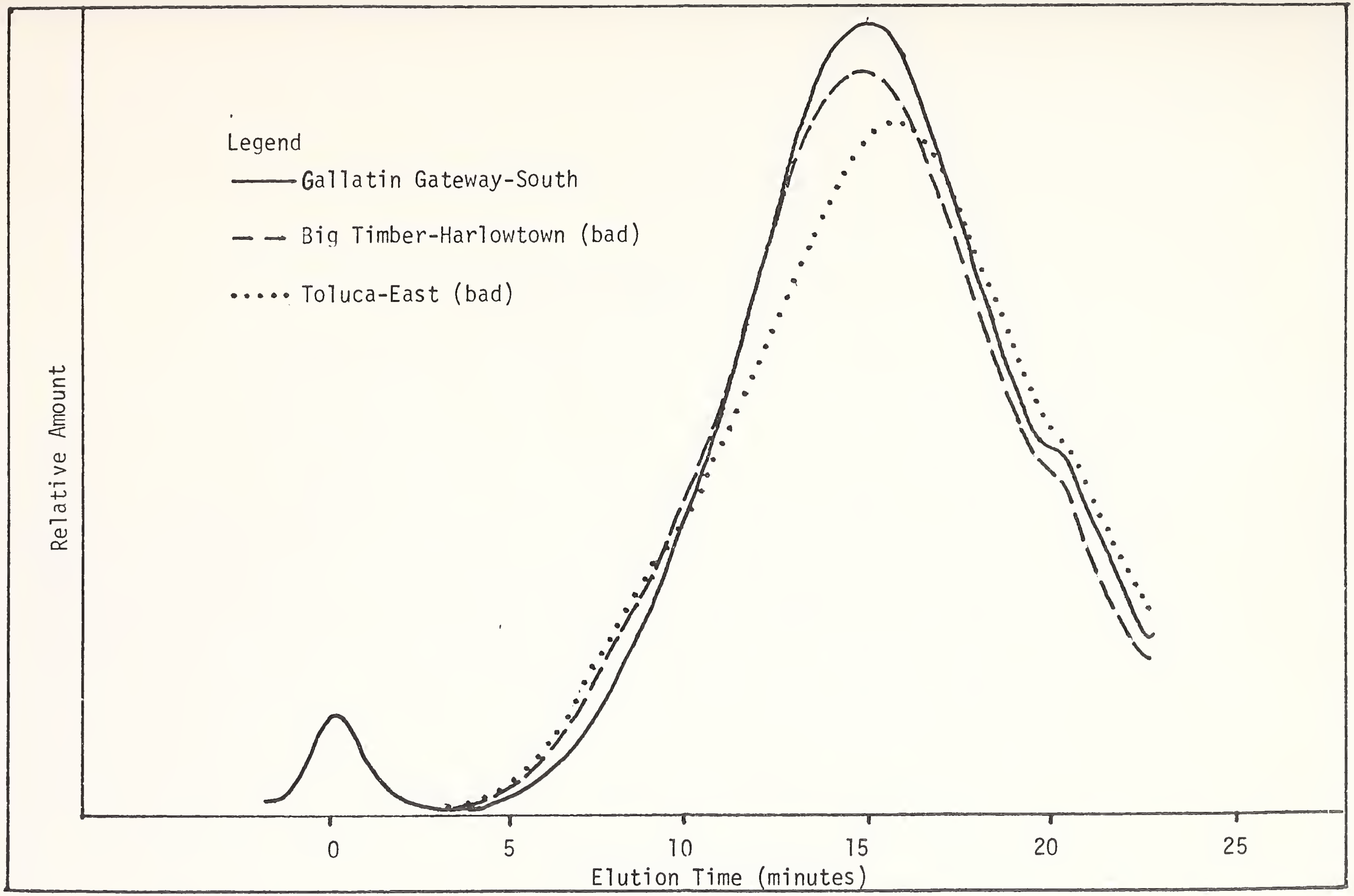

Figure 4. Established roadways, 85-100 design penetration.

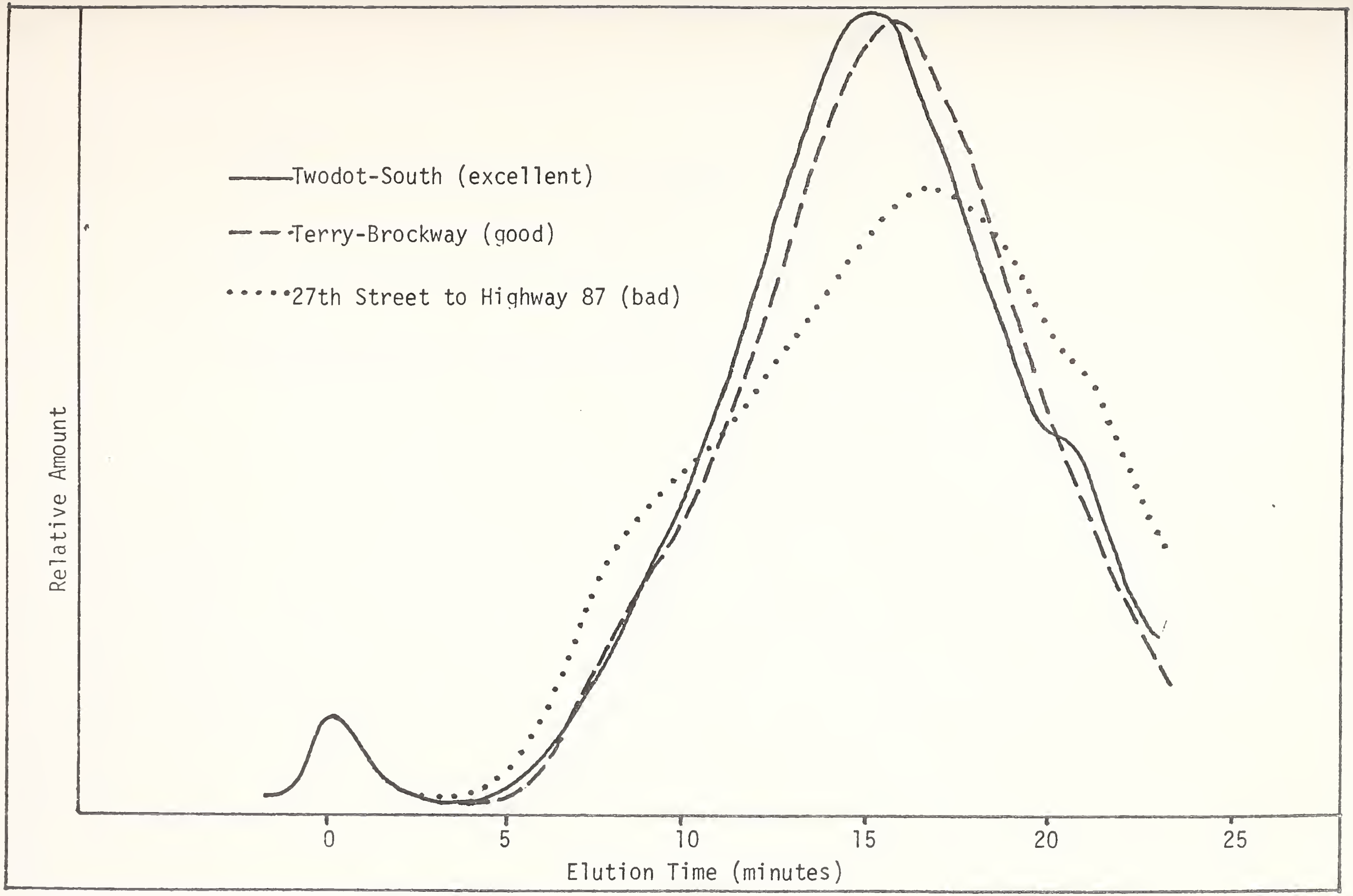

Figure 5. Established roadways, 100-120 design penetration.

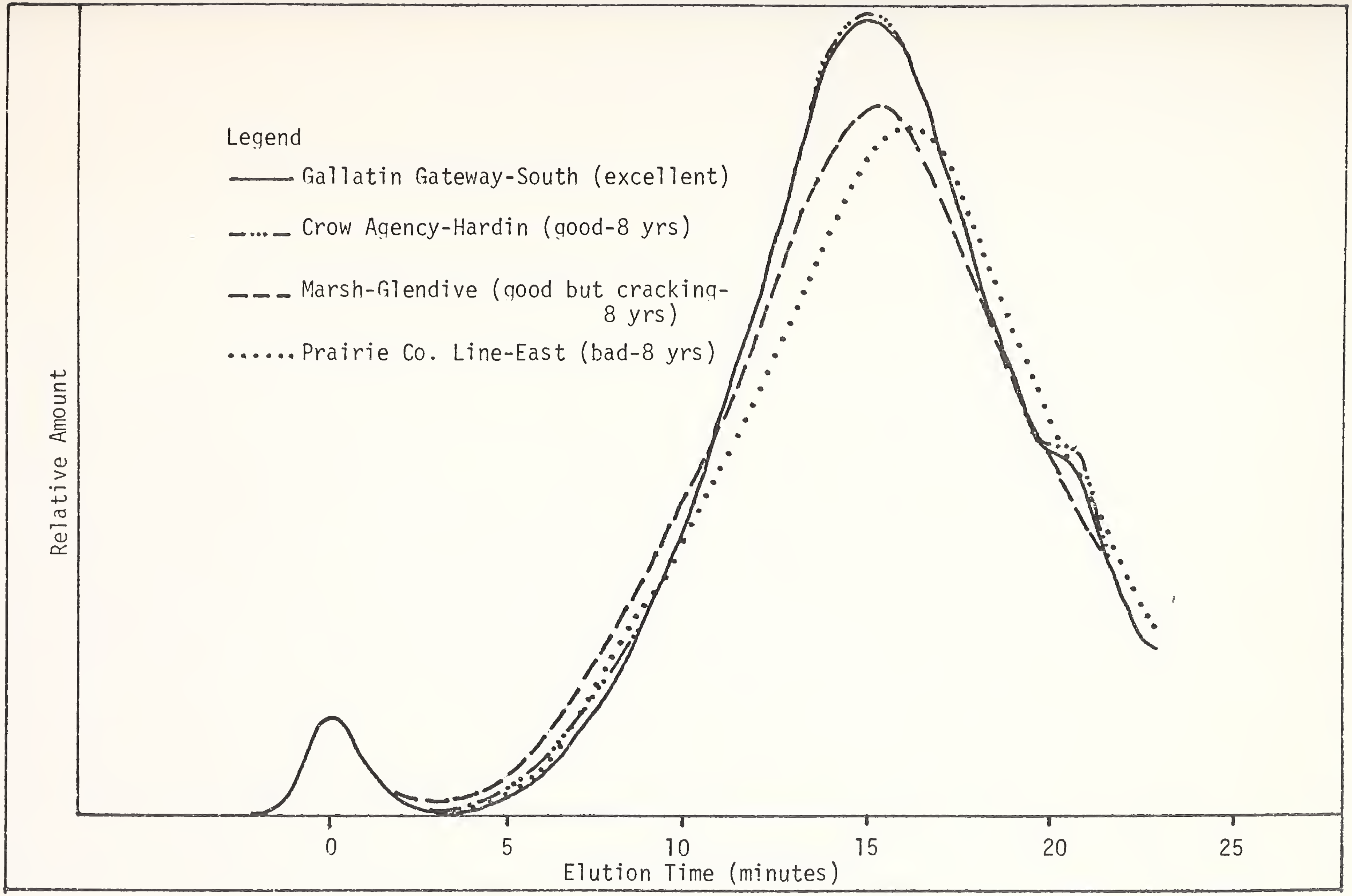

Figure 6. Established roadways, 120-150 design penetration.

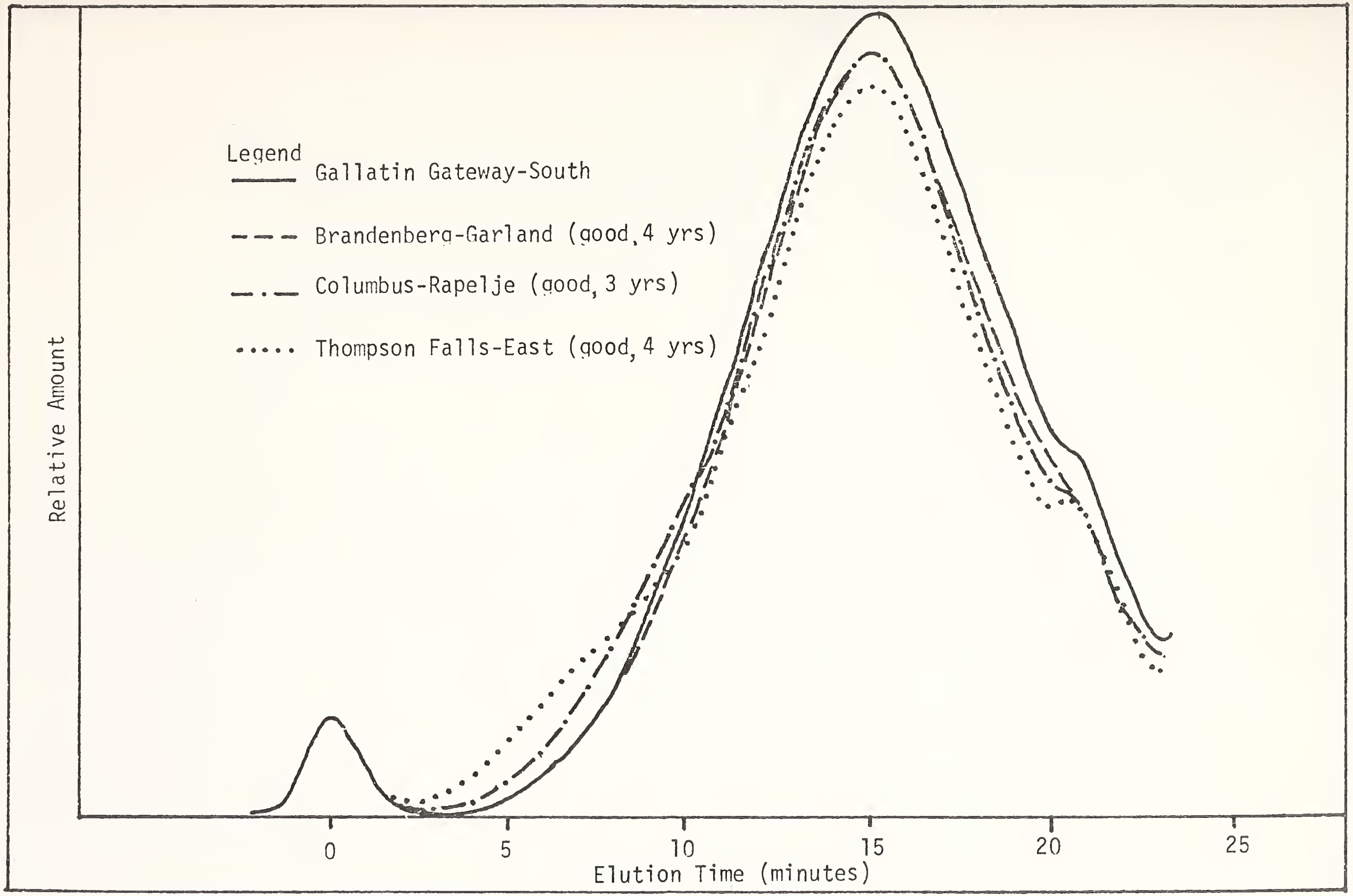

Figure 7. Established pavements, 200-300 design penetration.

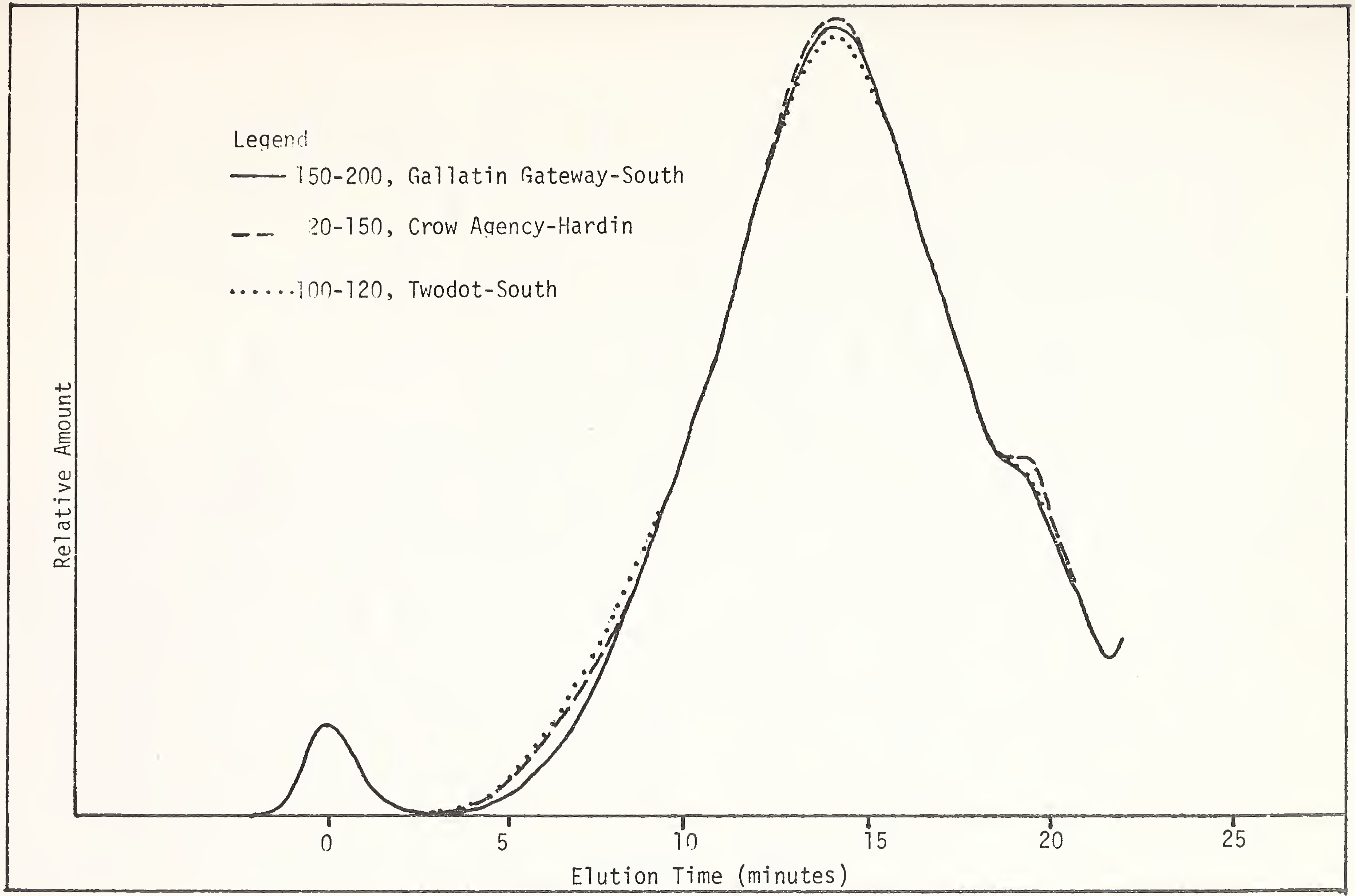

Figure 8. Best roads from various design penetrations.

differences are minor and are confined mainly to the LMS region. It is also apparent that the increase in size and quantity of the LMS region varies with penetration value. That is, the softer asphalts contain fewer and smaller LMS components. In summation, it is appropriate to use Gallatin Gateway-South as a standard for all penetration grades, within the confines of this study.

The trend established by study of figures 3-6 is that the greater the disparities between a given asphalt and Gallatin Gateway-South, the poorer the performance of that asphalt. This is especially true with respect to the size and amount of LMS material. This is, asphalts which contain considerably more and/or larger LMS components are more likely to crack under conditions found in Montana.

With this in mind, it is expected that the Crow Agency-Hardin road (figure 6) will continue to perform well. The same may be said for the Brandenberg-Garland road (figure 7). However, the fate of two other roads in figure 7 is more in doubt. Both Columbus-Rapelje and Thompson Falls-West contain considerably more LMS materials than Gallatin Gateway-South; the LMS components in the Thompson Falls-West asphalt are very large. Thompson Falls-West contains only 13% asphaltenes,* which might mitigate the effects of the LMS components for a short time. Columbus-Rapelje contains 18.7% asphaltenes, which can only aggravate the effects of the LMS components. In short, both

* See section IV.D. for a discussion of the role of asphaltenes.

of these roads are likely to prove to be disappointing.

D. *The value of asphaltenes vs HPLC analyses.*

Earlier work had indicated that asphalt quality was a function of analyzed asphaltene percentage. It is now known from established road analyses that all samples containing more than 19 percent asphaltenes were obtained from bad roads. Eighteen asphalts containing 15 percent asphaltenes or less were from good to excellent roads, with only 2 exceptions. Asphaltene percentages between 16 and 18 were split between good and bad asphalts. Therefore, the percentage of asphaltenes as obtained by the Corbett-Swarbrick method is a fair mirror of asphalt performance. However, it is not accurate when used alone. Figure 9 demonstrates this point. In that figure are chromatograms of two asphalts, one "bad" and one "excellent". The "bad" asphalt contains 17.4% asphaltenes, the "excellent" asphalt contains 17.8% asphaltenes. However, it is obvious from the chromatograms that these asphalts are not alike. In the LMS region, Drummond-East contains considerably more and larger LMS materials than Twodot-South. There is also a slight shift in the elution time of the curve maximum toward the LMS for Drummond-East relative to Twodot-South. In other words, Drummond-East is, overall, composed of larger materials and contains considerably more and larger LMS components than Twodot-South. These facts not only explain the failure of the Drummond-East asphalt but also demonstrate that HPLC can give information about an asphalt that is not shown by asphaltene analyses.

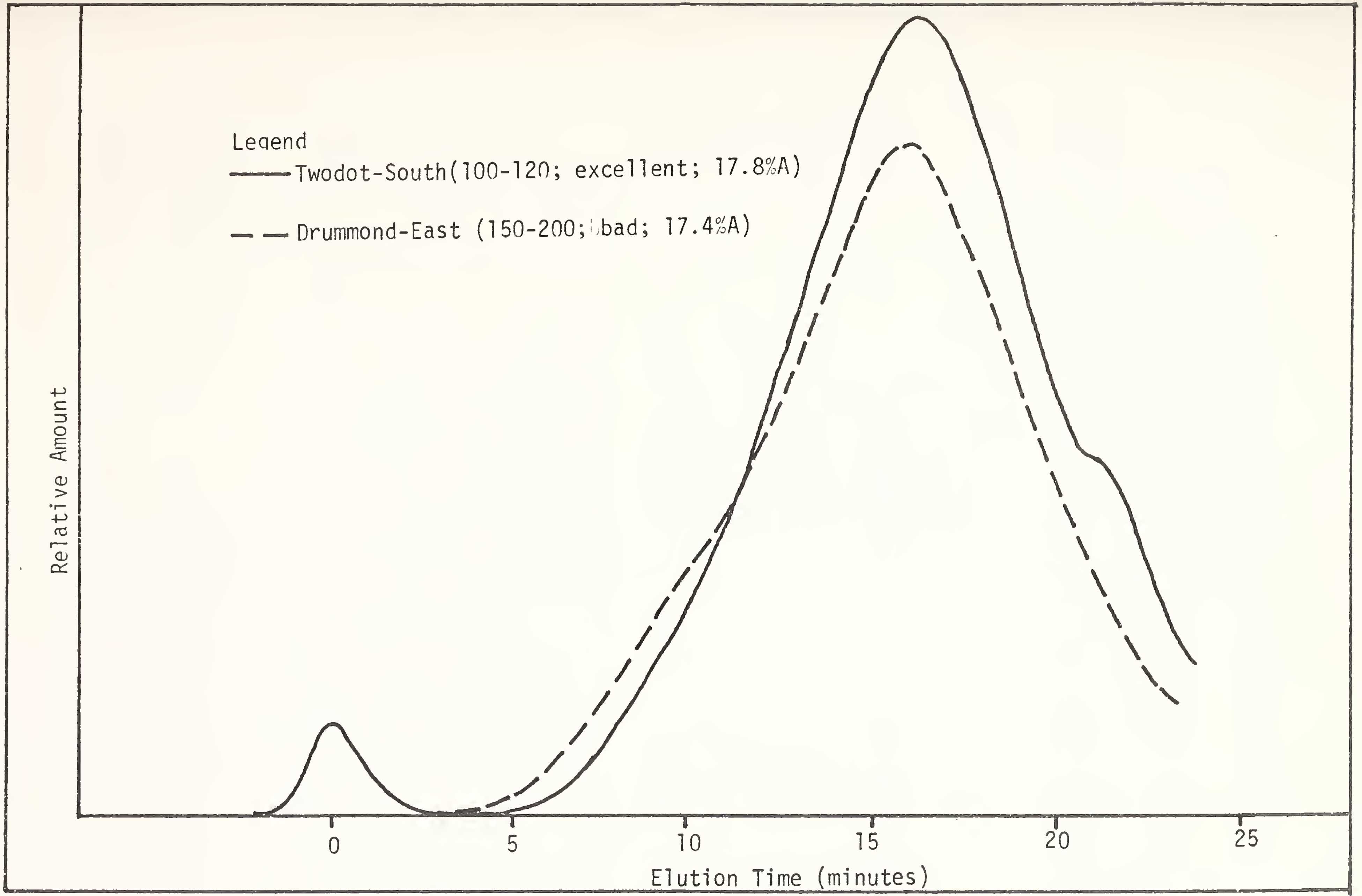

Figure 9. Comparison of asphalts with similar asphaltenes concentrations.

E. Correlating penetration and ductility data with performance of established roadways.

In order to demonstrate any relationship between roadway performance and penetration and ductility* values of the recovered asphalts, the ranges of values in each quality category are gathered in Table 4.

Table 4

Roadway Quality	Penetration (77°F)	Ductility, cm. (40°F)
Excellent	62-120	9.0-52
Good	46-209	4.5-100
Poor	44-58	2-8
Bad	28-75	0.5-15

This data shows that penetration and ductility of such samples are, at best, only fair indicators of asphalt quality. This is due, in part to the nature of such physical tests. It is believed that laboratory processing does not artificially harden or soften samples. (See page 6). (Trichloroethane has been reported to harden asphalts. However, it was not used in this study).

The possibility that asphalts of one particular design penetration grade might maintain original penetration better than another grade

*Penetration and ductility values of the extracted asphalts were determined by the Montana Department of Highways.

led to assembly of the data in Table 5.

Table 5

Original pen	85-100	100-120	120-150	150-200	200-300
Current range	44-58	28-62	35-138	22-120	94-210
decrease	32-56%	38-77%	0-77%	20-89%	0-69%

There is no overwhelming superiority of one design penetration class in its ability to maintain penetration.

The next step was to determine if asphalts from one refinery were better able to maintain original penetration. Table 6 lists the penetrations at sampling time of some asphalts in the 120-150 class by refiner. In general, asphalts from refiner C have maintained their design penetration better than those from refiner B.

Table 6

Penetration at sampling of 120-150 grade asphalts

	Refiner		
Age	B	C	D
3 years	62	-	-
6 years	92	105	-
8 years	57	138	-
8 years	72	-	-
8 years	90	-	-
10 years	-	68	105
10 years	-	111	-

The number of samples available was insufficient to permit a rigorous statistical treatment.

F. *Summary of findings concerning established roadways.*

At the beginning of this section (IV) it was stated that there was a two-part goal for the study of established roadways:

1. To determine the characteristics of asphalts from "excellent" roads;

2. To determine the ways in which less successful asphalts differ in these characteristics.

A variety of factors have been considered in making these determinations. Some of these have already been discussed and will be summarized later. Still other factors were found in the wealth of data included in Table 2. These factors will be discussed briefly in the next four paragraphs.

Roadways differ in the type of processing used in their construction (e.g., batch plant or continuous plant commonly used for these older roads) and in the type of filler (e.g., lime or fly ash) used , if any. In this sampling, no correlation could be discerned between success or failure of the roadway and either processing or fillers used.

Roadways also differ in the refinery source of the asphalt. It is difficult to make statistical correlations between roadway performance and refinery source of asphalt considering the limited number of samples analyzed and the subjective nature of the "good-bad" classification. However, it must be said that mats constructed with asphalt

from refinery C were consistently good to excellent, whereas those from refinery B were judged good to poor and, very frequently, bad, As stated in Section E, asphalts from refinery C seem to retain their design penetration better than those from refinery B.

Reasons for the superior performance of asphalts from refinery C may now be found in section III. It will be recalled that refinery C produces asphalt directly from the vacuum distillation unit, whereas refinery B produces asphalt via the PDA process and blends to meet penetration specifications. It may be concluded that, although crude source probably had an effect on asphalt quality, the better asphalts were made by treating the crude "gently" and controlling penetration by crude mixture and conditions in the vacuum distillation tower. On the other hand, it appears that the propane deasphalting process frequently resulted in low quality asphalt in the past. Whether PDA processing will continue to have this effect is open to question in light of the character of current crude oils.

The practice of blending SMS materials (e.g., gas oil, etc.) into harder asphalts certainly enables penetration requirements to be met. It is not able to correct the problems associated with excessive amount and/or size of LMS components, however.

In conclusion, for established roadways:

1. There is no definitive correlation between roadway quality and type of processing plant, filler, or ductility or penetration of the asphalt at sampling time.

2. There is a general correlation between performance of the asphalt and type of processing used at the refinery.

3. There is fair correlation between the performance of the asphalt and the percentage of asphaltenes it contains. The ideal range of asphaltenes content is 12.5 to 16.5%. (See pp. 10 and 31).

4. There is good correlation between the performance of the asphalt and the shape of the HPLC chromatogram. Gallatin Gateway-South asphalt has been selected as representative of asphalts which have given excellent performance in Montana. The extent to which the chromatogram of an asphalt differs from that of Gallatin Gateway-South is proportional to the extent to which that asphalt has failed (or will fail).

V. THE CHANGES IN ASPHALT DUE TO MIXING WITH AGGREGATE, LIME OR FLY ASH: THE 1978 ROADS.

Before discussing the subject of this section, a new and superior technique for analyzing chromatograms must be described. This technique in no way alters the HPLC method. It simply replaces the Soltec strip-chart recorder (which was used for all chromatograms presented up to this point) with a microprocessor called a "Data Module" (Waters Assoc.). This instrument produces a chromatogram similar to those previously seen (figure 10). It's superiority lies in the additional information it makes available (Table 7).

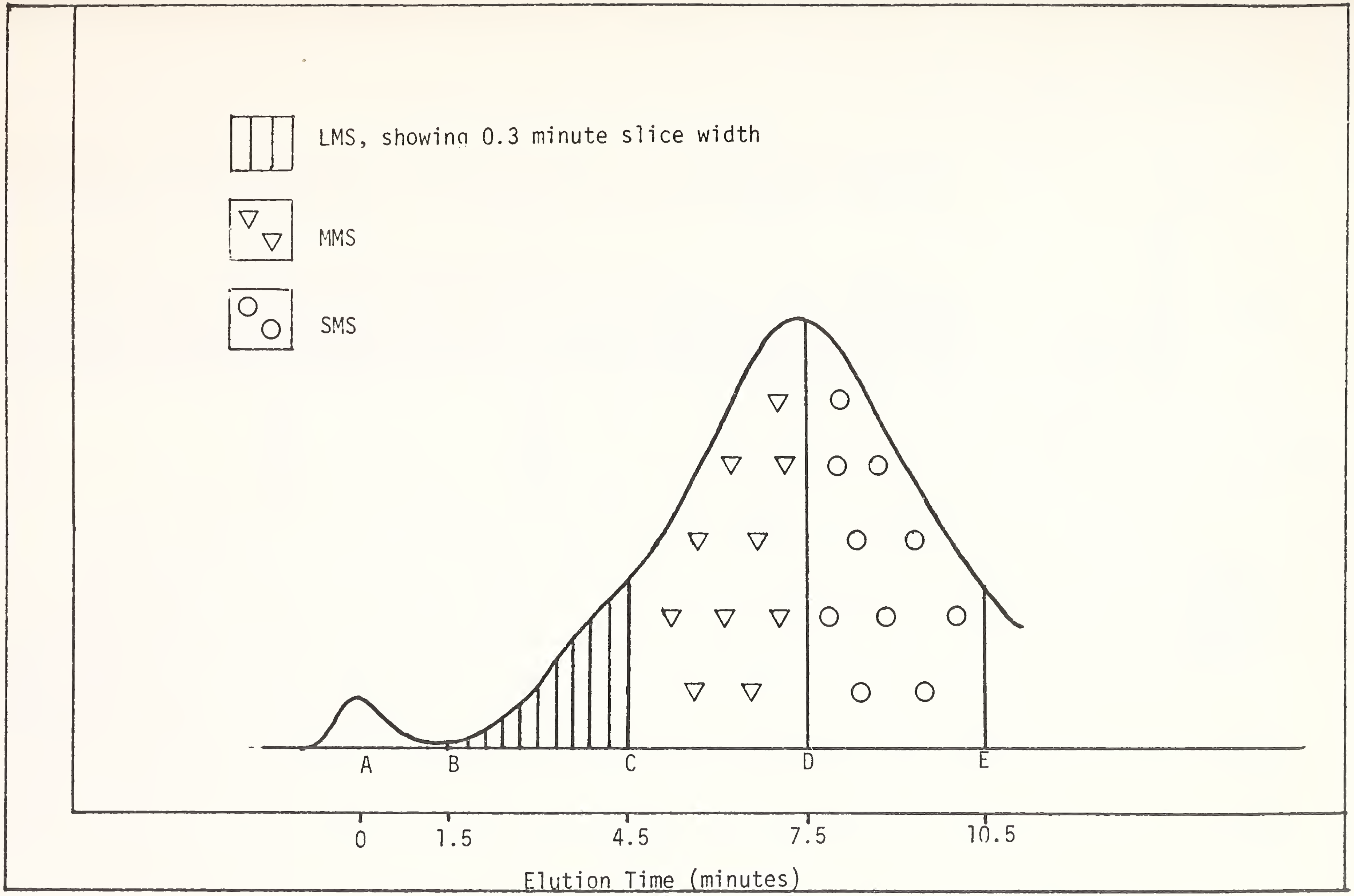

Figure 10. Example of Data Module-generated chromatogram.

Table 7

JAN. 3, 1980   03:00:04   CHART- .0 CM/MIN
RUN #16   CALC #1
COLUMN   SOLVENT   OPR ID:

GPC QUANTITATION

RT	AREA		
18.17	595600		
18.47	4975780		
18.77	9684550		
19.07	8322760		
19.37	4572580		
19.67	2241090		
19.97	1067390		
20.27	732200		
20.57	900200		
20.87	1616790		
21.17	2600290		
21.47	4114580		
21.77	6268870		
22.07	8972550		
22.37	12522700		
22.67	16480400		
22.97	21219900	754283	7.0%
23.27	26393300		
23.57	32197800		
23.87	38769100		
24.17	46166900		
24.47	54228000		
24.77	62634500		
25.07	69786300		
25.37	74453400		
25.67	75894900		
25.97	74305400	5548308	51.7%
26.27	70183500		
26.57	64461600		
26.87	58232300		
27.17	51898300		
27.47	45832800		
27.77	40240100		
28.07	34911400		
28.37	29938500		
28.67	25564200		
28.97	21831600	4430947	41.3%
29.27	18391500		
		10733538	

The Data Module provides a measure of the total area under the curve by measuring the area of slices 0.3 minutes wide. This is diagrammed in figure 10 between B and C. The elution time for each slice is printed on the chromatogram.* The area under that portion of the chromatogram which represents asphalt (from B to D) has been divided into three sections, each 3 minutes wide, corresponding to large molecular size (LMS), medium molecular size (MMS) and small molecular size (SMS) components. The percentage of each component is easily calculated from the printout associated with each chromatogram (Table 7). This data in conjunction with the analyzed percentages of asphaltenes and with visual comparison of the chromatograms may then be related to asphalt quality.

This method of data analysis will now be applied to the 1978 roads. Samples were obtained from nine roadways constructed during 1978. These samples consisted of the oil,** plant mix (asphalt-aggregate mixture from the batch or drum dryer type plant) and a core,

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*It may be noted that the elution times for a given component differ between these chromatograms and those used in earlier portions of this paper. This results from use of different pumping rates and chart speeds and does not affect the validity of the data. However, when comparing chromtograms, only those run under identical conditions may be used.

**For the purposes of this study, "oil" will be used when referring to the asphalt cement as obtained form the refiner.

all corresponding to the same section of roadway. These projects with pertinent data are listed in Table 8.

In nearly all cases, processing in either batch plant or drum dryer type plant resulted in a change in the LMS region. Figures 11-17, in which the chromatograms for asphalts before and after processing* are superimposed, are representative of these cases. This change indicated that processing results in slight increases, both in size and amount, of LMS components.

Although these changes were small for the whole asphalt--1.2 to 4.2 percent--they represent significant changes in the LMS region--increases of 20 to 80 percent. This additional material in the LMS components evidently arises from polymerization of smaller components.

The amounts of asphaltenes in these samples by Corbett-Swarbrick analyses also showed small changes, ranging from negligible to 4.7% of the whole asphalt. However, these changes translate to as much as a 45% increase in asphaltenes. The LMS area percentages increased more than did the asphaltenes percentages. This further demonstrates that asphaltenes are not the sole contributors to LMS components (see page 10). This is even more evident in the case of Sidney-Culbertson-2 in which the LMS region increased while there was a 4.1% decrease in asphaltenes (figure 18a). The reason for the decrease is not obvious.

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*The "oil" represents the asphalt before processing, whereas, "core" represents the asphalt after processing, ie., extracted from a core sample.

Table 8 1978 Roadways

Identification	Refiner	Additives	Plant Type	Sample Type	% Asphaltenes	% * LMS	% * MMS	% * SMS	Pen 77° F	Ductility cm. 40° F
85-100 Design Penetration Class										
38.' Broadway at Helena, Butte	A	-	Batch	Oil[a]	14.4	7.7	52.3	40.0	-	-
M 5816(3)				Core[b]	15.4	7.7	53.0	39.3	40	4.25
				Difference[†]	+1.0	0.0	+0.7	-0.7		
39.' U. S. #2-Havre-East	D	-	Batch	Oil	15.3	10.1	51.4	38.5	-	-
F 1-6(2)382				Core	14.2	12.4	49.7	37.8	98	4.75
				Difference	-0.9	+2.3	-1.7	-0.7		
120-150 Design Penetration Class										
40.' McDonald Pass-East	B	-	Batch	Oil	13.2	6.4	51.6	42.0	-	-
RF-FF 249(27)				Core	13.0	7.7	50.7	41.6	75	31.5
				Difference	-0.2	+1.3	-0.9	-0.4		
41.' Melville-N & S	B	1.5% hyd. lime	Drum	Oil	10.4	5.1	46.5	48.5	-	-
F 54-1(1)15				Core	15.1	9.3	48.3	42.4	65	16
				Difference	+4.7	+4.2	+1.8	-6.1		
42.' Sidney-Culbertson-2	B	-	Drum	Oil	13.4	6.0	49.6	44.4	-	-
F 62-1(2)1				Core	9.3	7.2	50.5	42.4	128	55
				Difference	-4.1	+1.2	+0.9	-2.0		
43.' Two Medicine Bridge-East	D	-	Batch	Oil	14.6	8.0	48.2	43.8	-	-
RF-FLH 353(15)				Core	14.5	9.7	50.1	40.2	118	20.5
				Difference	-0.1	+1.7	+1.9	-3.6		
44.' Wolf Point-SE	A	1% fly ash	Drum	Oil	13.6	8.5	48.4	43.1	-	-
F-FLH 25-2(2)47				Core	13.5	10.7	47.7	41.6	80	9.5
				Difference	-0.1	+2.2	-0.7	-1.5		
200-300 Design Penetration Class										
45.' Big Sandy-Rudyard	B	-	Batch	Oil	8.7	5.8	50.3	43.9	-	-
RS 432-1(2)27				Core	10.0	7.5	50.9	41.6	124	-
				Difference	+1.3	+1.7	+0.6	-2.3		
46.' Sidney-Culbertson-1	B	-	Drum	Oil	12.1	5.8	49.6	44.6		
F 62-1(2)1				Core	12.9	8.7	49.6	41.7		
				Difference	+0.8	+2.9	0.0	-2.9		

* see figure 10

† value for oil subtracted from value for core

' indicates both Soltec and Data Module spectra are included

a asphalt cement as obtained from refinery

b asphalt recovered by extraction from core

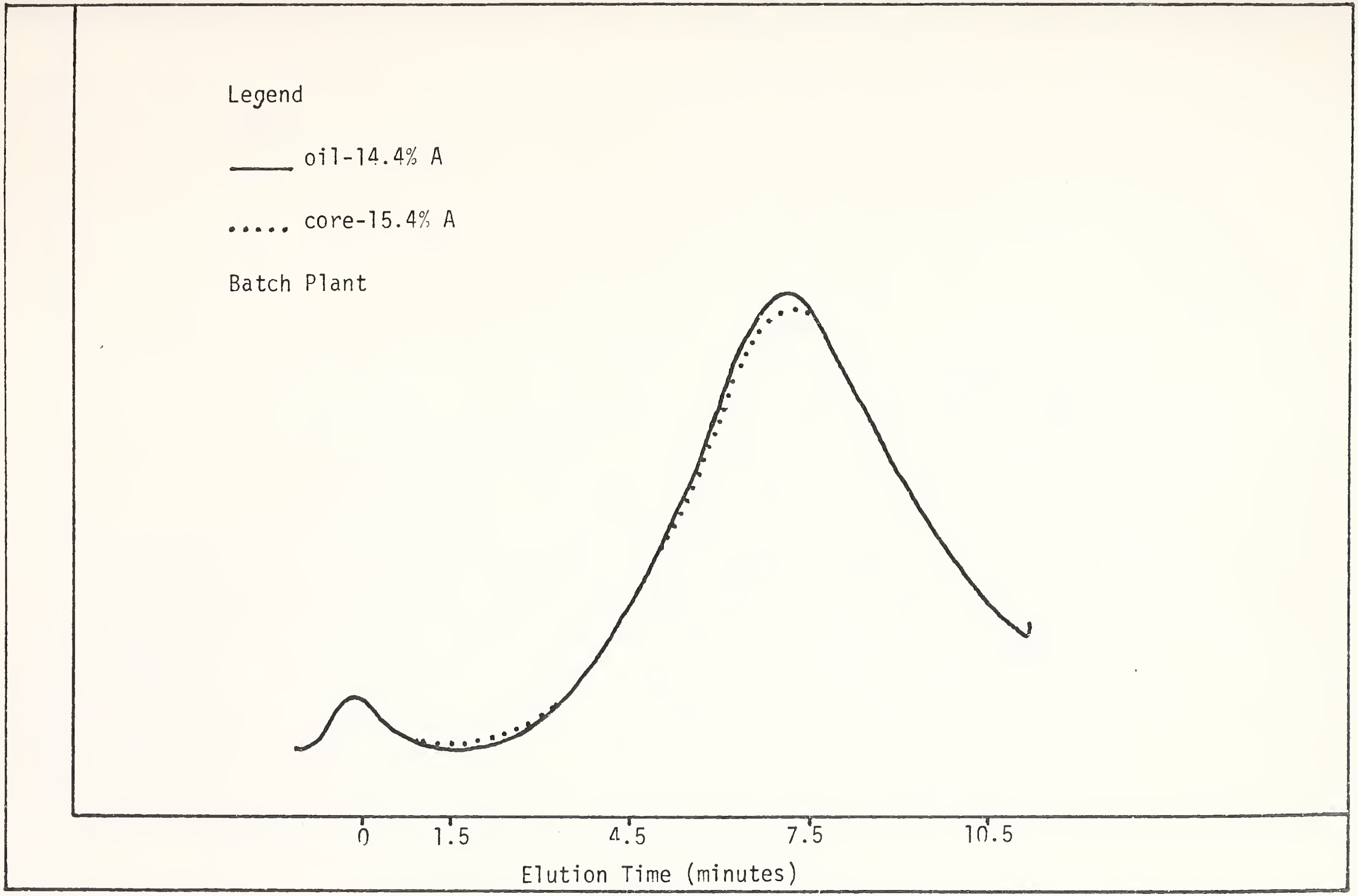

Figure 11. Broadway at Helena, Butte (85-100/Refiner A).

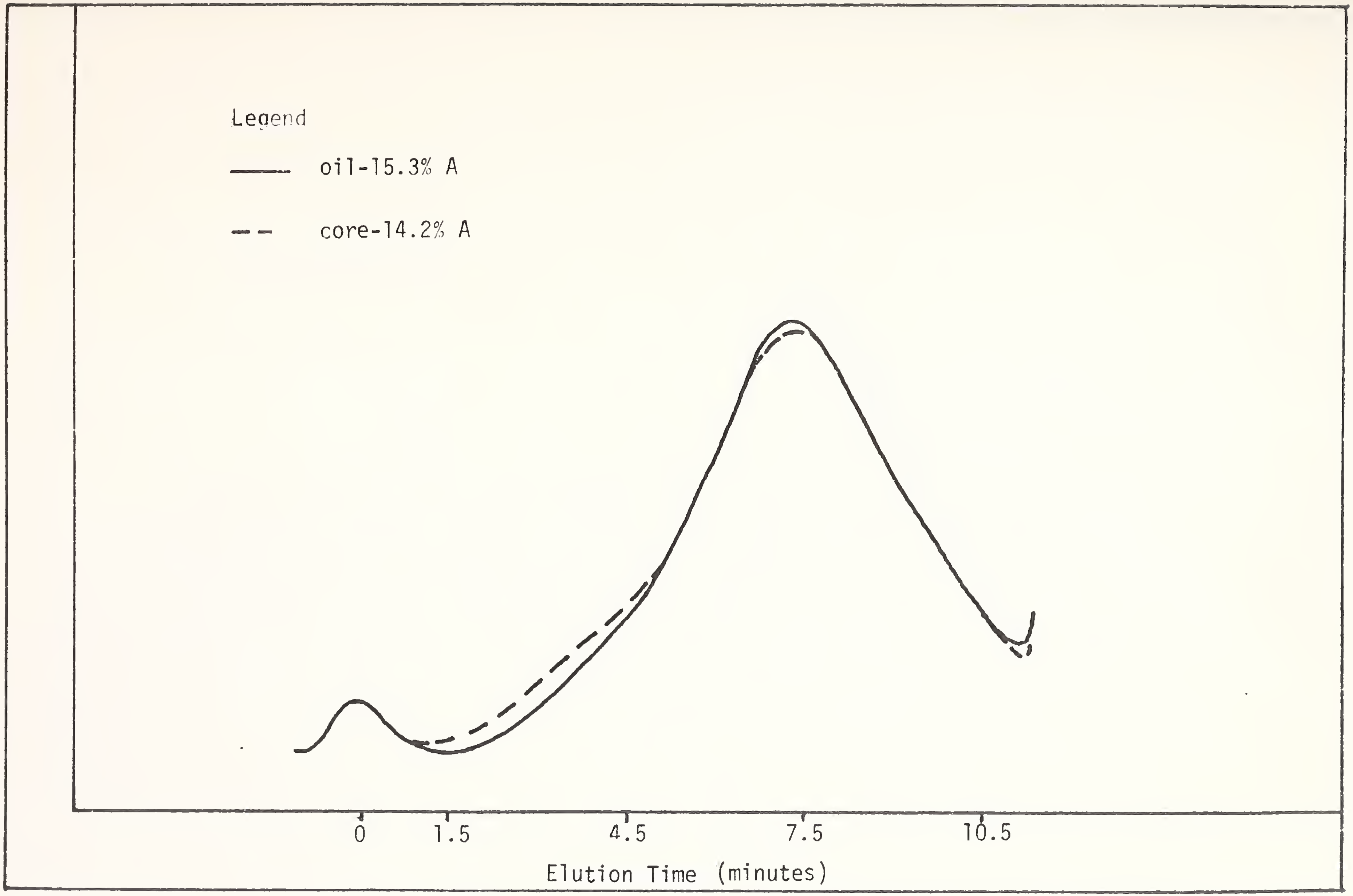

Figure 12. U. S. #2 Havre-East (85-100/Refiner D).

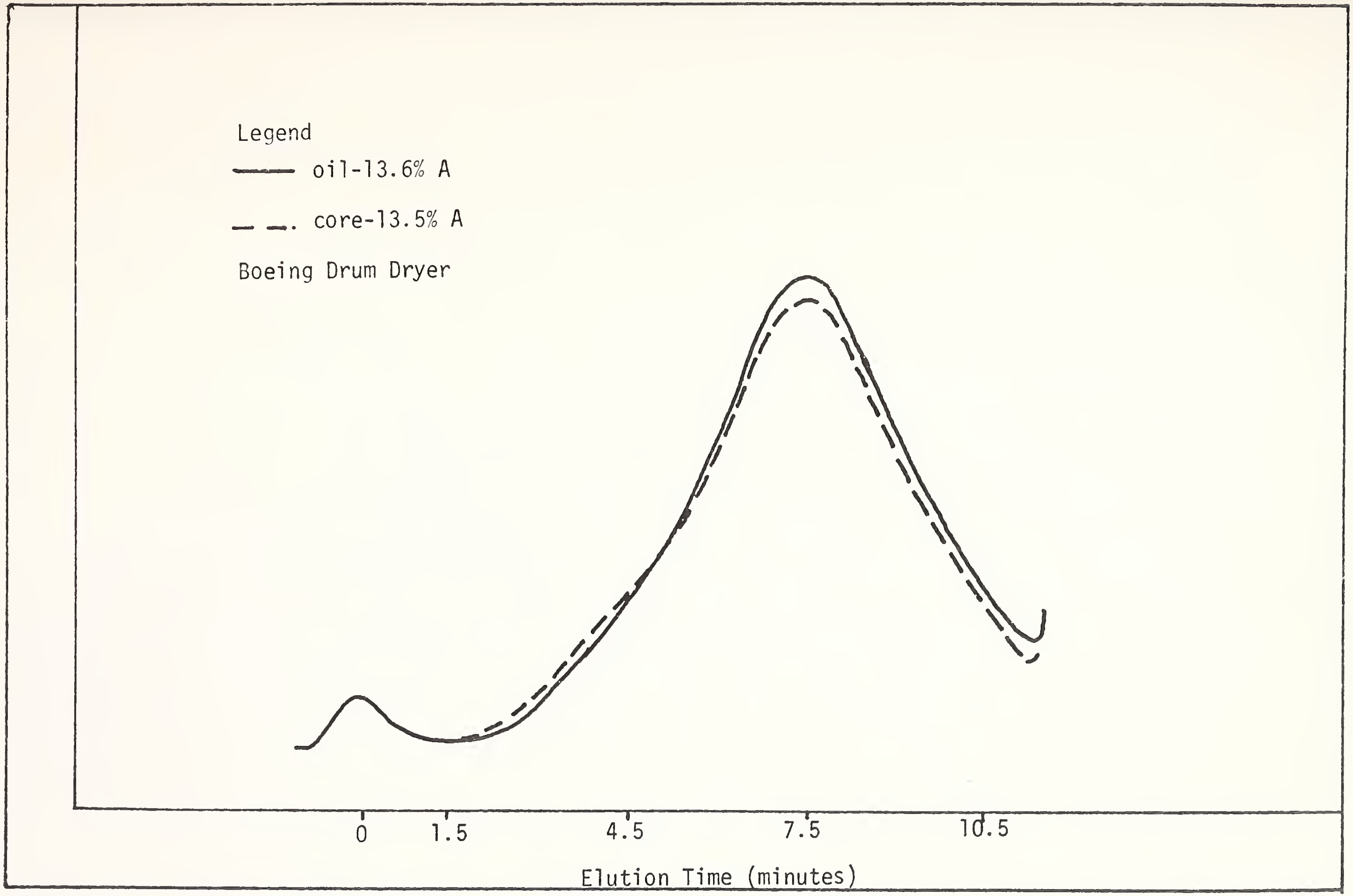

Figure 13. Wolf Point- SE-1 (120-150/Refiner A).

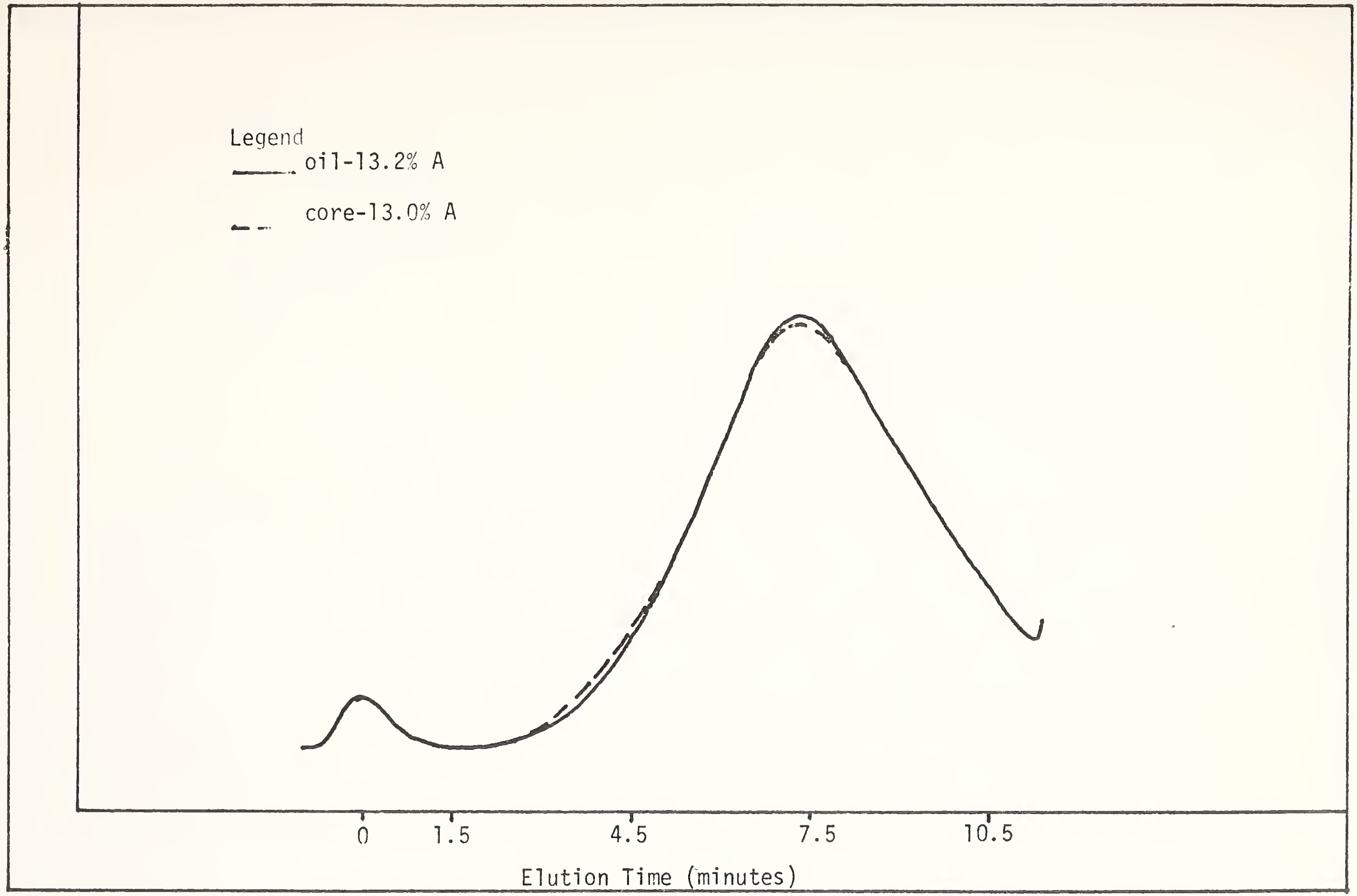

Figure 14. McDonald Pass-E & W (120-150/Refiner B).

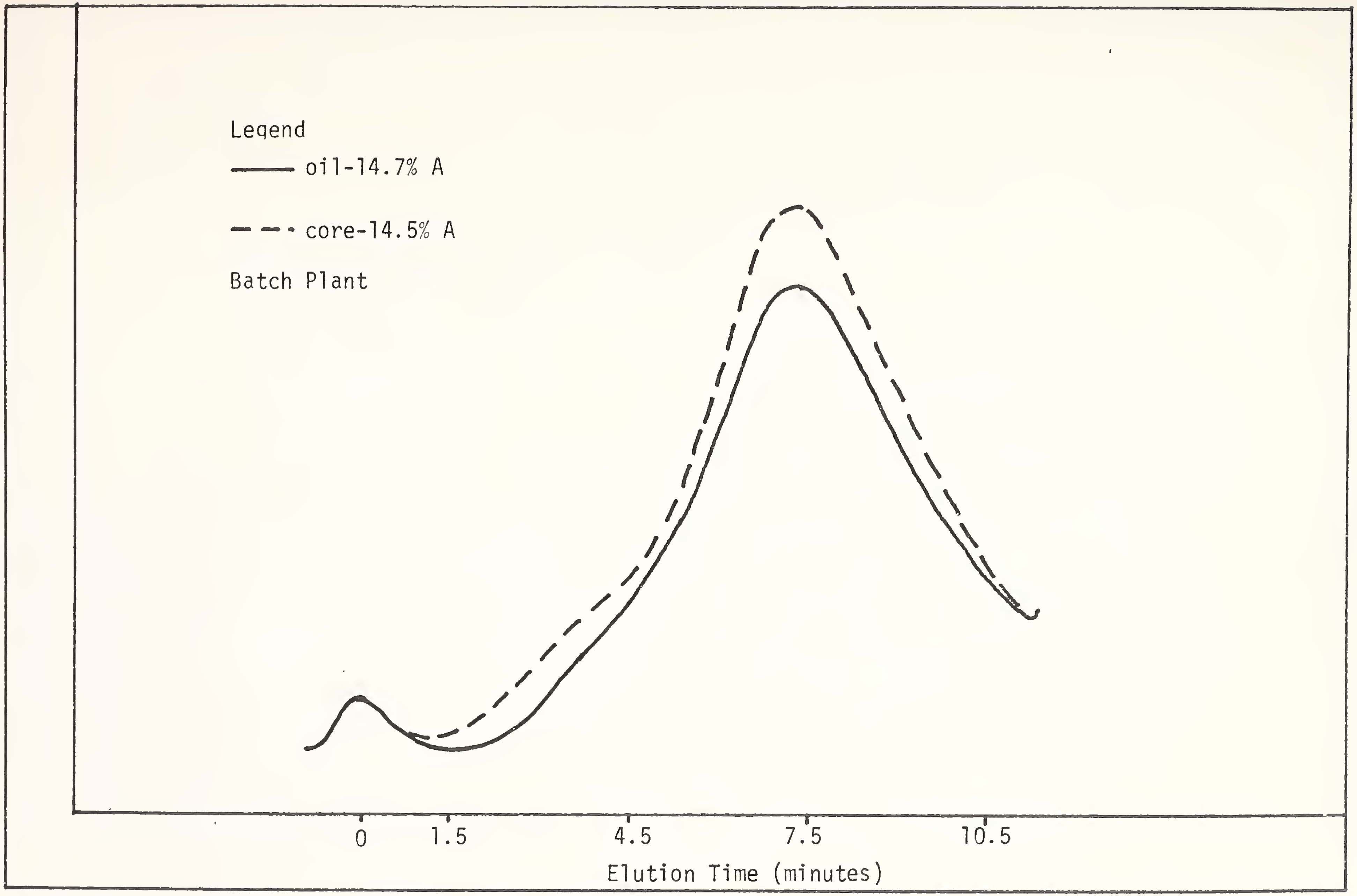

Figure 15. Two Medicine Bridge-East (120-150/Refiner D).

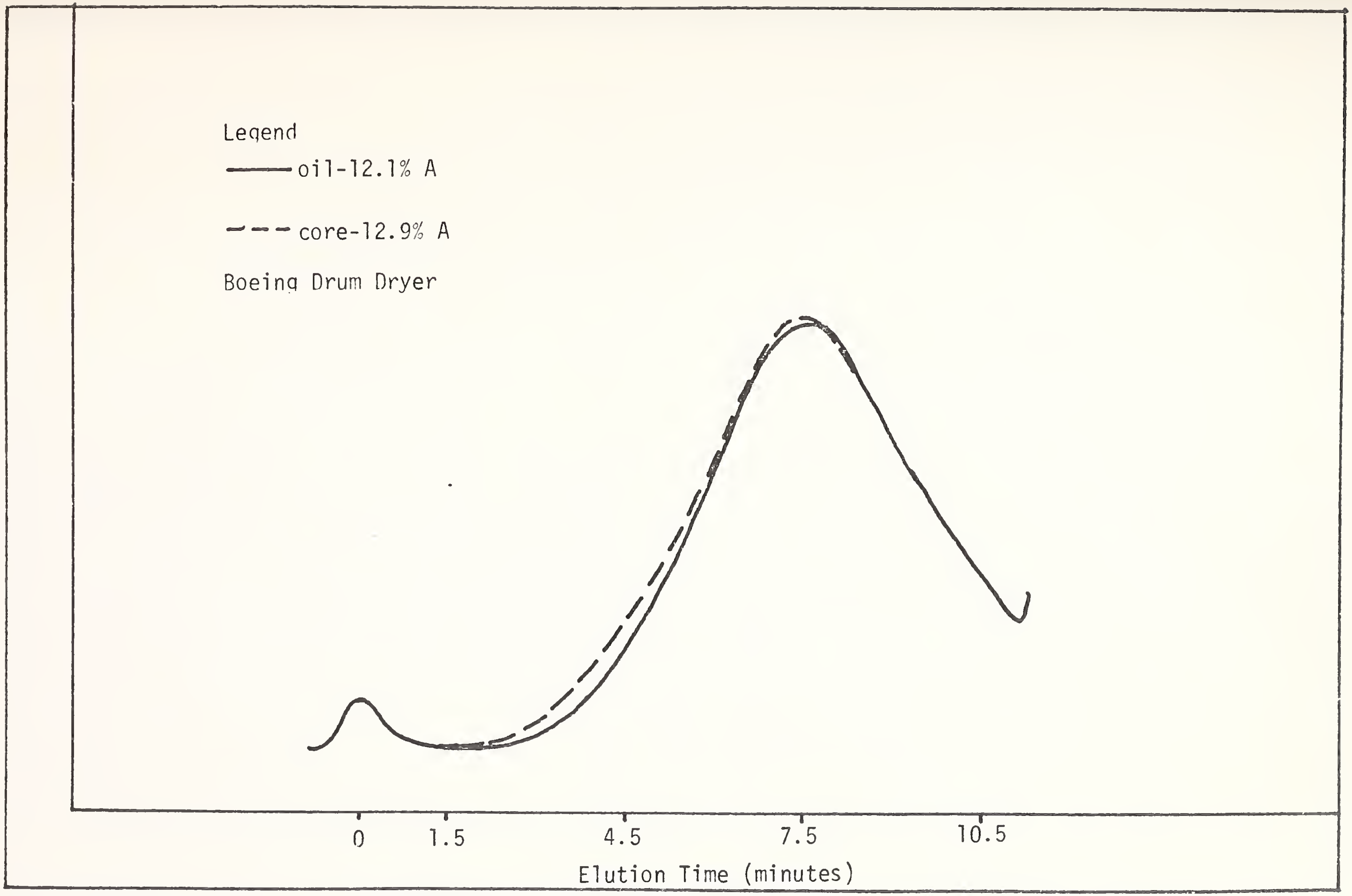

Figure 16. Sidney-Culbertson-1 (200-300/Refiner B).

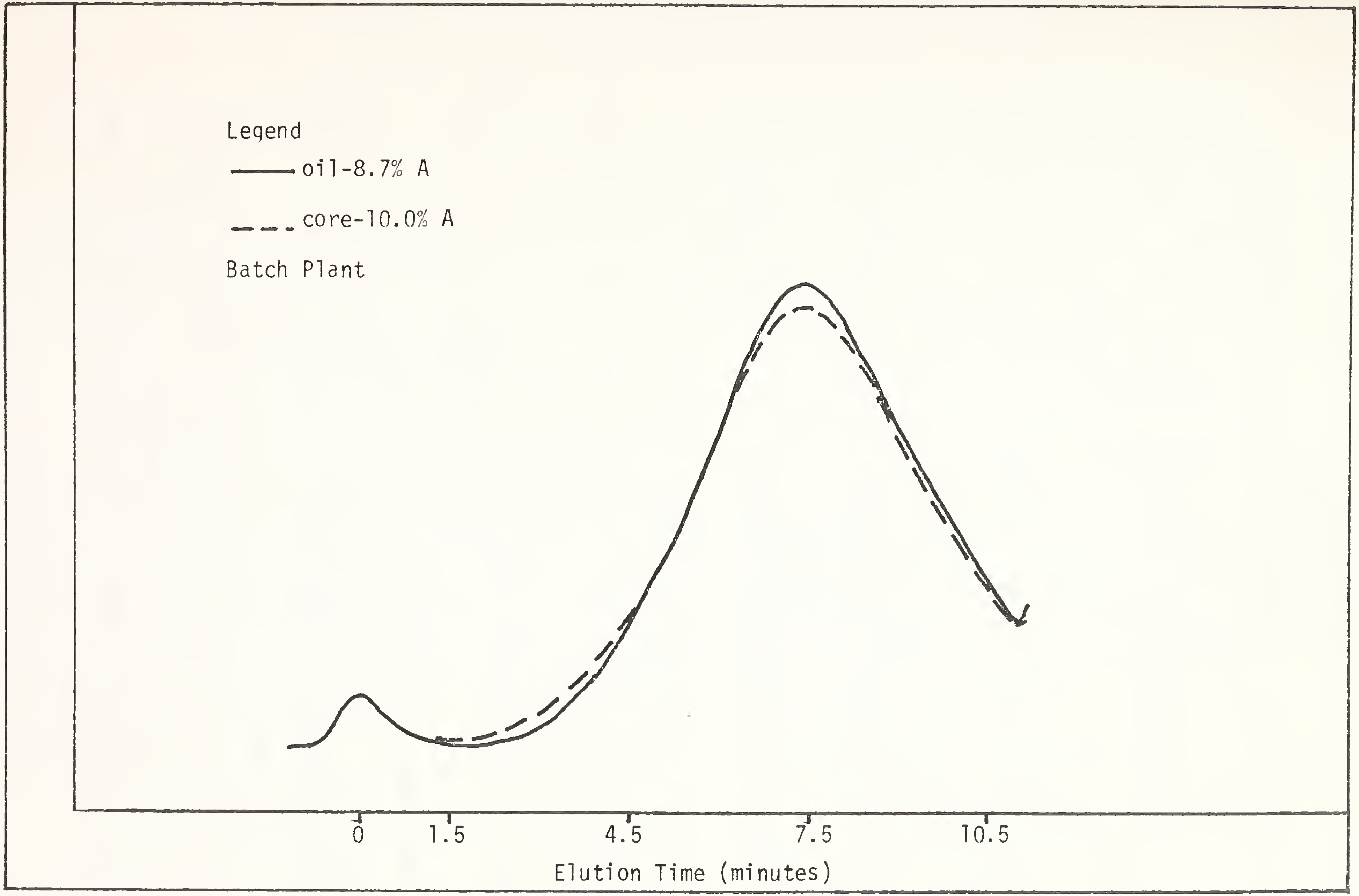

Figure 17. Big Sandy-Rudyard (200-300/Refiner B).

In figure 15 for Two Medicine Bridge-East, visual comparison shows an apparently large change in the asphalt as a result of processing. This change is not substantiated by asphaltenes analysis or by area percentages. In such cases it must be understood that the height of the curve, and, therefore, the area under it, are functions of the amount of sample injected into the system. However, the ratio of a certain slice of the area to the whole area determined by Data Module is a constant for a given sample. Therefore, the area percentage from the Data Module may be relied upon to put such visual discrepancies into proper perspective. In this case, the area analysis shows a real but small difference between the two samples (Table 8).

Within the limits of the samples available, batch plant and drum dryer mixing do not appear to differ in their effects upon the asphalt. Similarly, there appears to be no difference in the response to processing of asphalts from individual refineries or of asphalts from the various penetration classes.

The greatest increase in LMS area (4.2%) and in asphaltenes content (4.1%) occurred in the Melville-N&S asphalt. Interestingly, this was the only asphalt of the 1978 group to contain hydrated lime. The difference in response to processing between Sidney-Culbertson-2 and Melville-N&S asphalts is shown in figures 18A and 18B, respectively. Both projects used asphalt from refinery B. Both were processed via drum dryer. However, no hydrated lime was

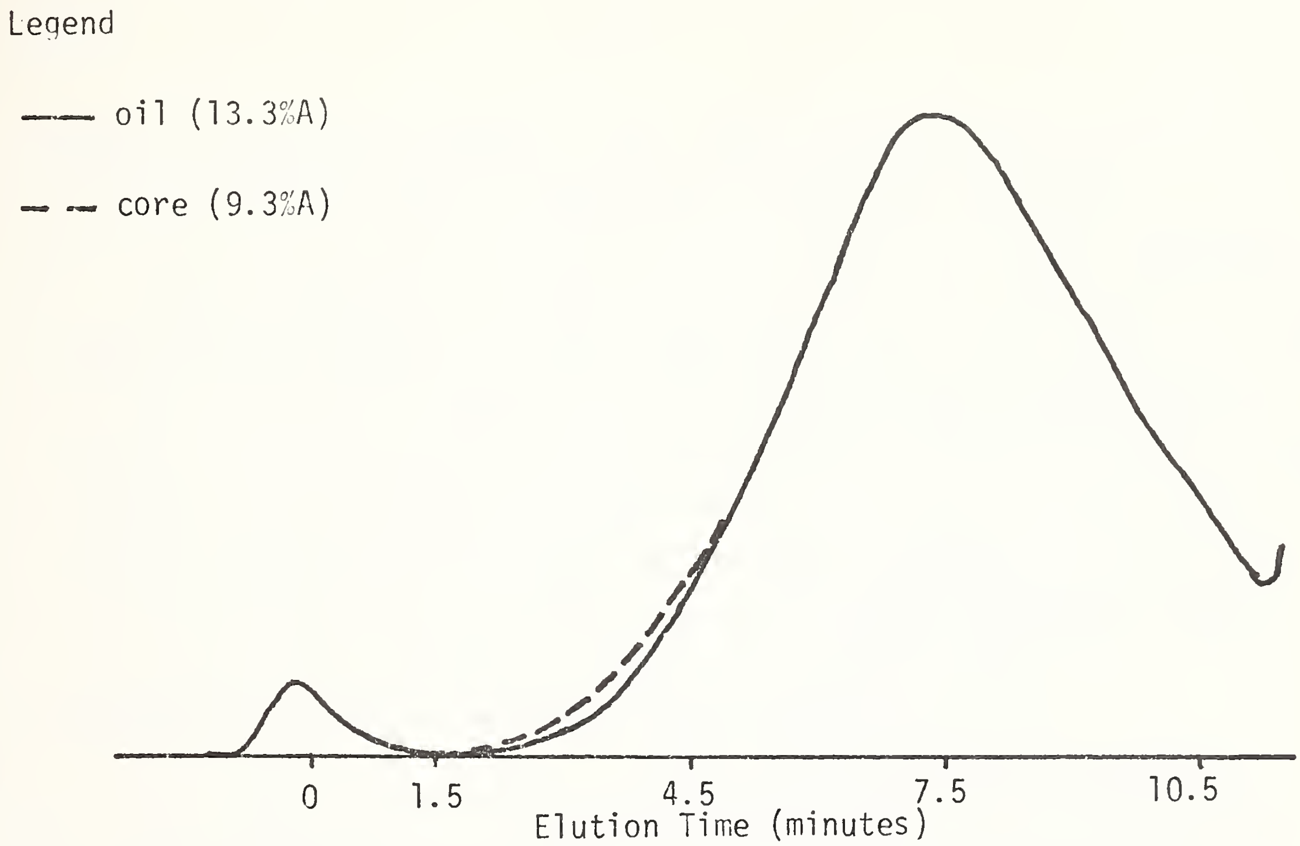

Figure 18A. Sidney-Culbertson-2 (120-150/Refiner B)

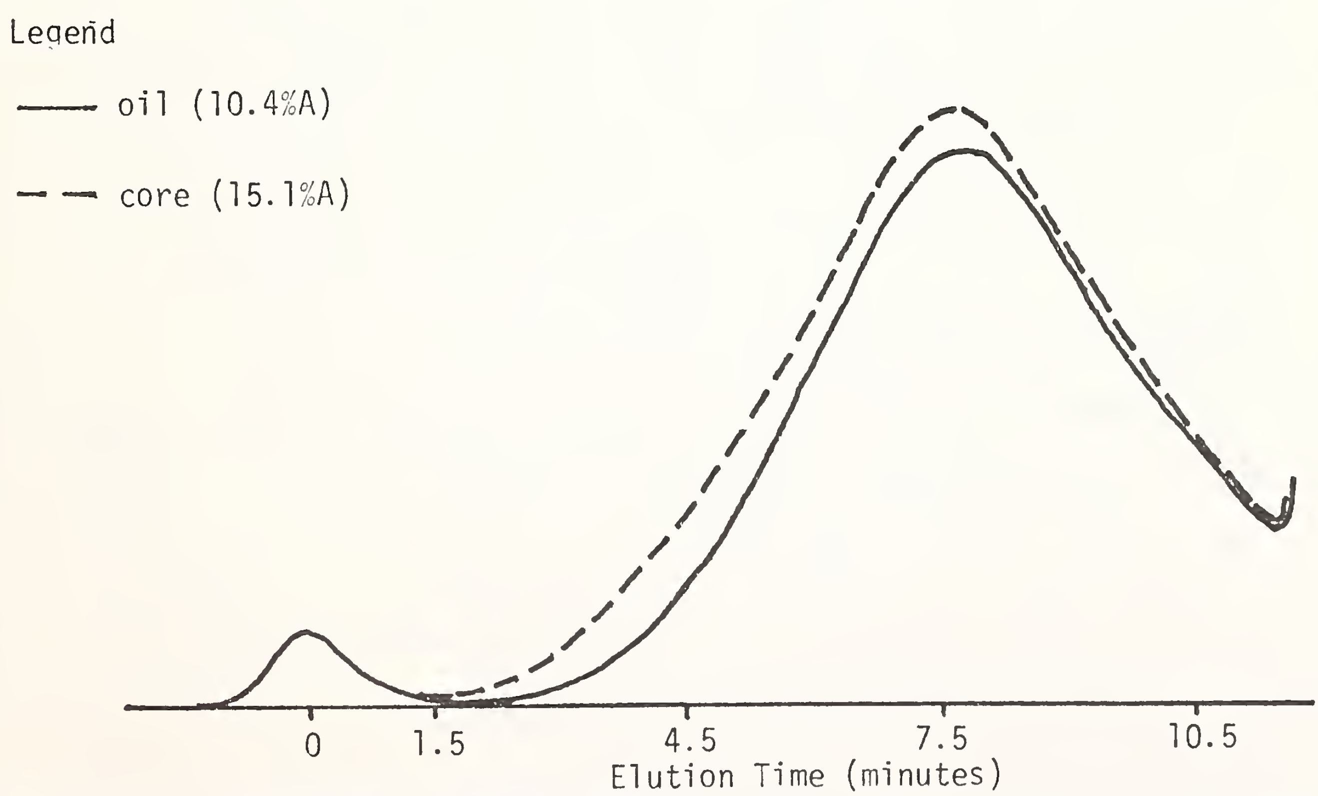

Figure 18B. Melville-N&S (120-150/Refiner B)

added to Sidney-Culbertson-2. The figure shows the proportionately greater change in LMS size and amount in the Melville asphalt.

Further inspection revealed that the Melville project had been divided into two sections. In the southern portion, lime was added during the mixing process, whereas no lime was used in the northern section. Refinery, mixing process and design penetration remained the same. The Soltec chromatograms for these two sections are shown in figure 19. It is clear that lime is responsible for a greater increase in LMS components than produced by drum dryer processing alone.

The implications of this discovery are potentially important, for they mean that the molecular size of asphalt can be engineered by the addition of lime. Further investigation is strongly warranted.

It should be emphasized that the changes discussed in the above paragraphs, although small, are real*. They demonstrate not only the effects of processing on asphalt but also the unique potential of HPLC in the analysis of a variety of factors effecting asphalt.

VI. ESTIMATING THE EFFECTS OF AGING

As implied in an earlier section, recent asphalts are probably quite different from older asphalts, mainly because of changes in crude oil supplies. However, very little is known about the original characteristics of older asphalts. Therefore, studies such as this project are hampered because there is little way to assess the real effects of aging on asphalts under actual roadway conditions.

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*The HPLC system used permits reproducibility of results within ±1%.

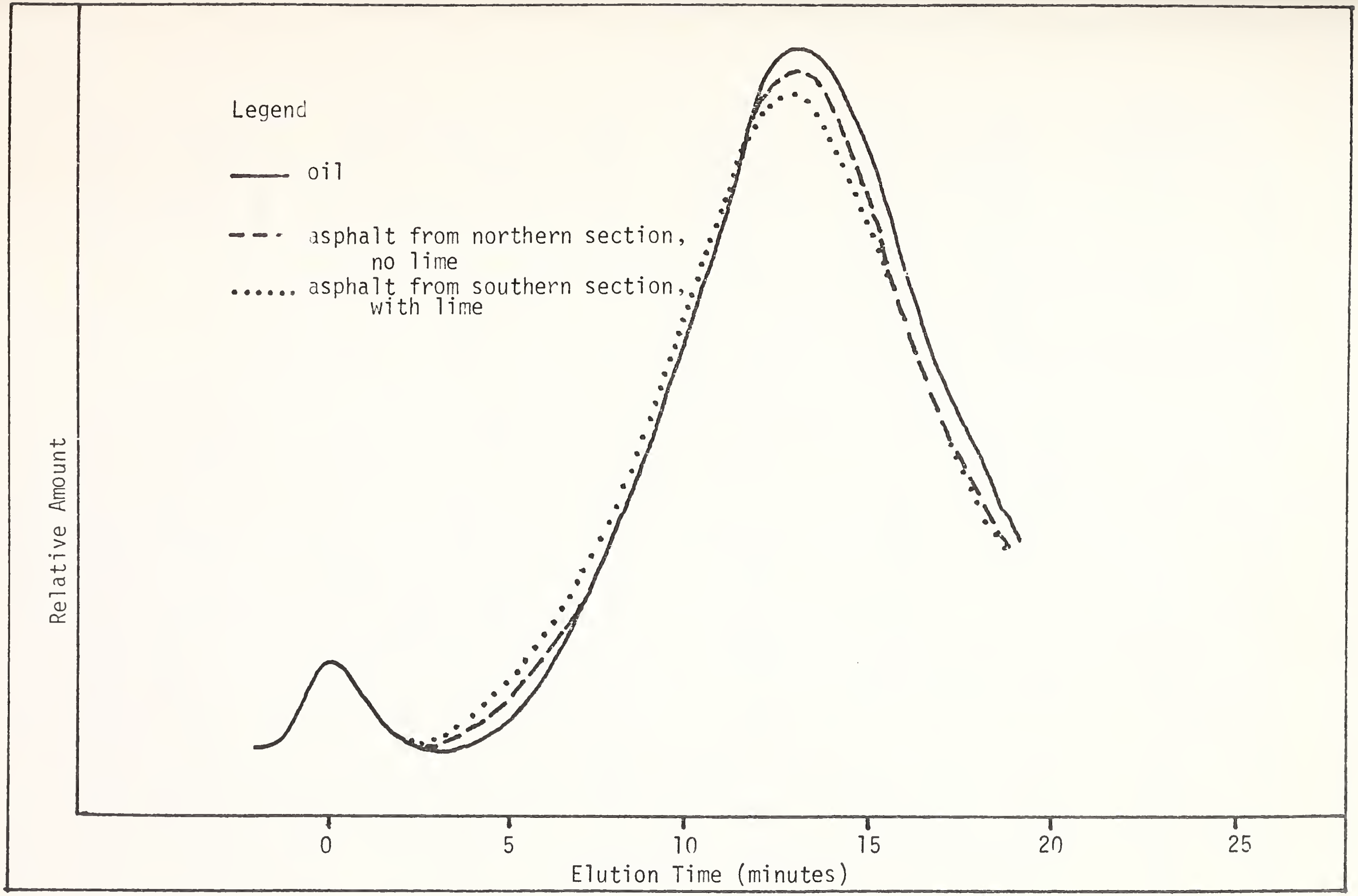

Figure 19. Soltec chromatograms of Melville-N & S oil and cores with and without lime.

A bank of current asphalt samples and a catalogue of their characteristics should be helpful in later assessment of the effects of aging. It is strongly urged that the catalogue resulting from the present study be continually updated.

It is clear from the preceeding section that the process of mixing with aggregate in either drum dryer or batch plant causes changes in the LMS region of the asphalt. These changes may be indicative of more drastic changes that would occur were the asphalt exposed to higher temperatures or for longer time periods. However, such conditions are not involved in asphalt processing and are, therefore of little concern. On the other hand, freeze-thaw cycles and the temperatures in the mat on hot summer days are of concern.

It is interesting to speculate on the history of an asphalt such as that from Circle-Glendive-2 (figure 20). Possibly the composition of the asphalt has not greatly changed since it was placed. In that case it may have been manufactured from a very heavy crude and/or been processed in the refinery to a very low penetration and then blended to pen specifications (150-200). These SMS additions may have since volatilized, leaving an asphalt that has failed.

Another possibility is that the composition has changed, some MMS components polymerizing to LMS, perhaps others breaking down under the effects of sun and weather. There are at least two problems with this theory. First, old but excellent roads such as Gallatin Gateway-South show no similar changes. Second, there are no middle-aged roads

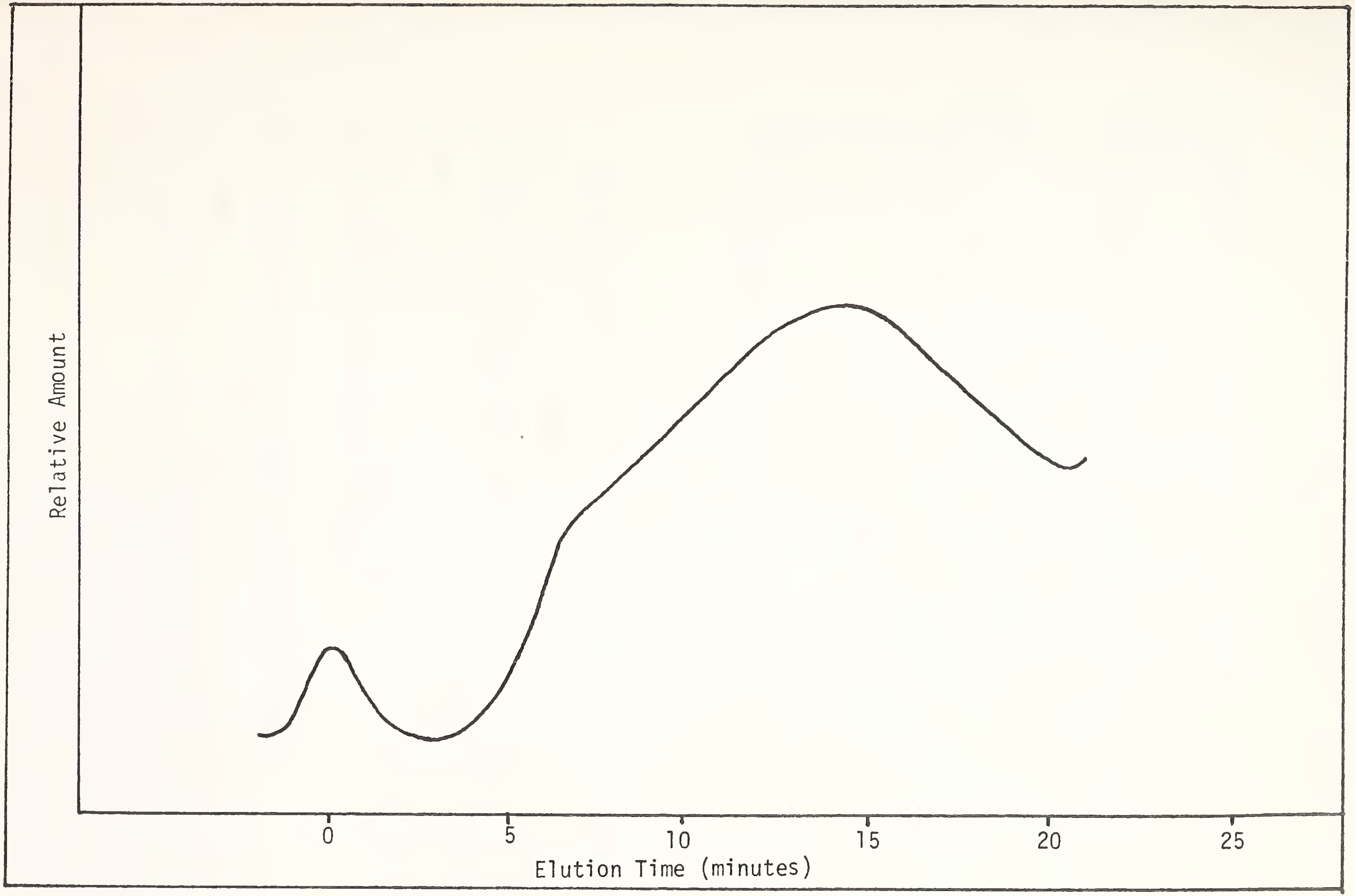

Figure 20. Circle-Glendive-2

which exhibit intermediate stages of such changes. There is, of course, a possibility that these changes have indeed occurred in this road, catalyzed by some factor in the aggregate, for example.

One road, Bozeman Pass-East, constructed in 1977, has been sampled again in 1979. The chromatograms are reproduced in figure 21. Visually, the 1979 core appears to have decreased in size and quantity of LMS components. This is confirmed by area analysis:

	%LMS	%MMS	%SMS
1977 core	11.4	47.5	41.1
1979 core	9.8	48.4	41.8

The asphaltenes, however, have increased:

1977 core - 11.7%

1979 core - 15.5%

One would like to conclude that changes in asphalt composition are minor with time. However, there is not enough data to warrant such a statement. Therefore, the characteristics of roadways at Big Sky, Bozeman Pass-East, as well as the 1978 and 1979 paving jobs discussed in this report should be followed in the course of any future work to firmly establish the effects of aging.

VII. CHARACTERISTICS OF A MODEL OF EXCELLENT ASPHALT

Based on the results which have been discussed in this report and the analysis of more than 90 different asphalt samples during the past several years, a model of high quality asphalt may now be proposed to the Montana Department of Highways. It is felt that asphalts which

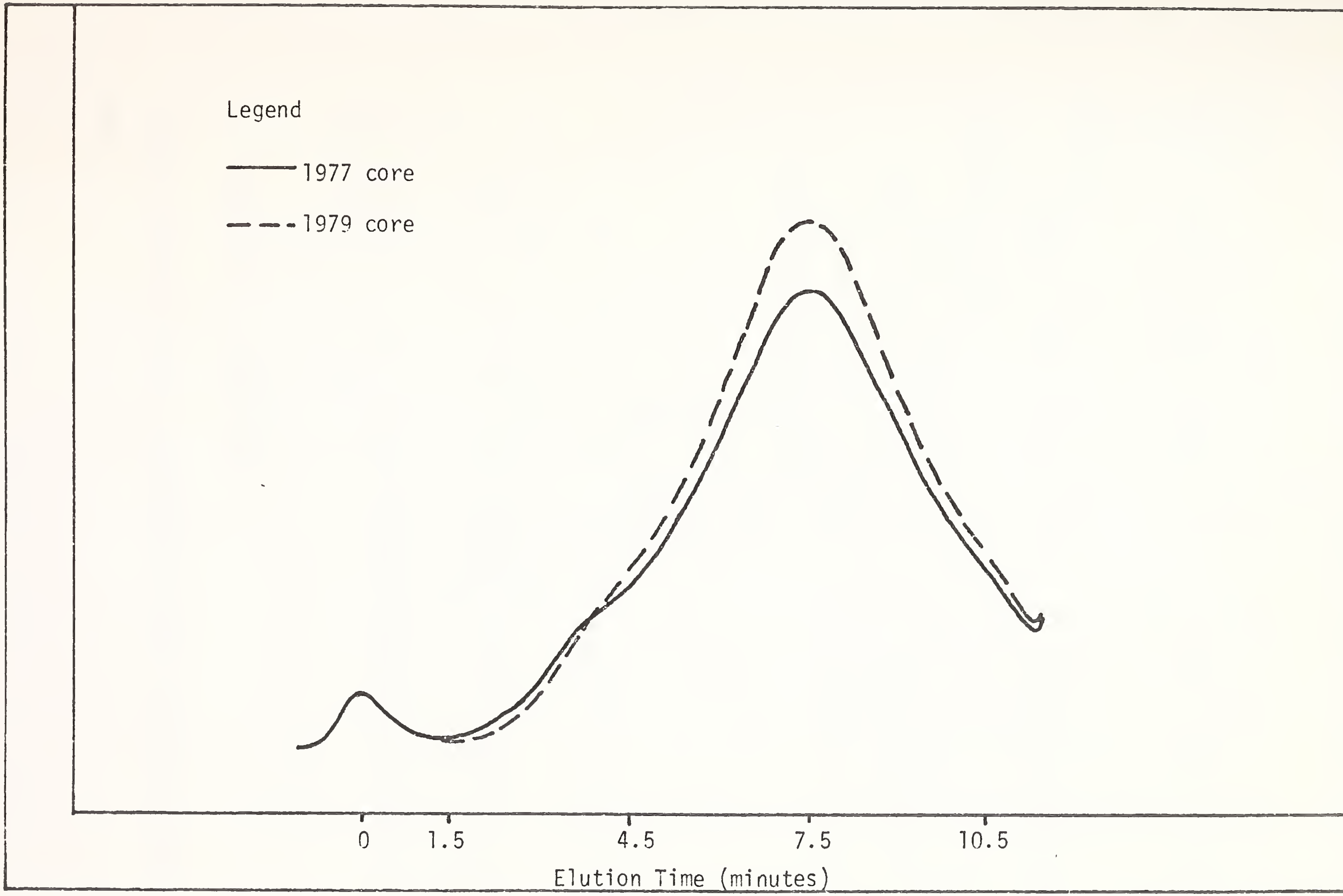

Figure 21. Bozeman Pass-East (120-150/Refiner A): comparison of 1977 and 1979 cores.

match this model closely will produce roadways which are successful both in durability and longevity under conditions found in Montana. Obviously, the performance of such a model is contingent upon the performance of other factors involved in roadway construction.

In order to give excellent service, an asphalt extracted from a finished pavement should show the following characteristics:

1. The HPLC chromatographic profile from a Data Module should mimic as closely as possible the curve shown in figure 22A.

2. The percentages of molecular size components should be within the following limits:*

LMS - 8-10%

MMS - 46-48%

SMS - 44-46%

3. The asphaltene content should be between 12.5 and 16.5%

4. Penetration should be above 120.

Bearing in mind that the percentages of the components of asphalts can be altered, or, perhaps even engineered, in the mixing process with aggregate or lime, the oil (asphalt before mixing) should have the following characteristics.

1. The HPLC chromatographic profile should be similar to that shown in figure 22B.

*Limits were derived from the analysis of best available asphalt pavements.

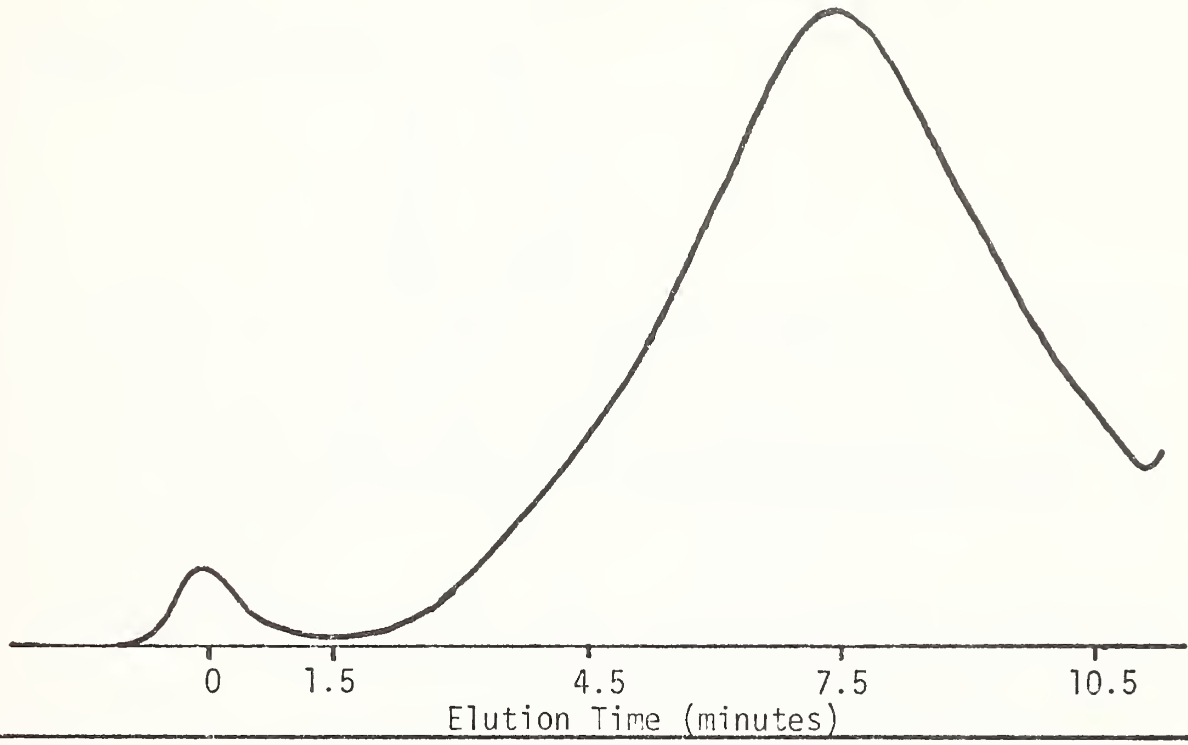

Figure 22A. Chromatographic profile of excellent asphalt from finished pavement.

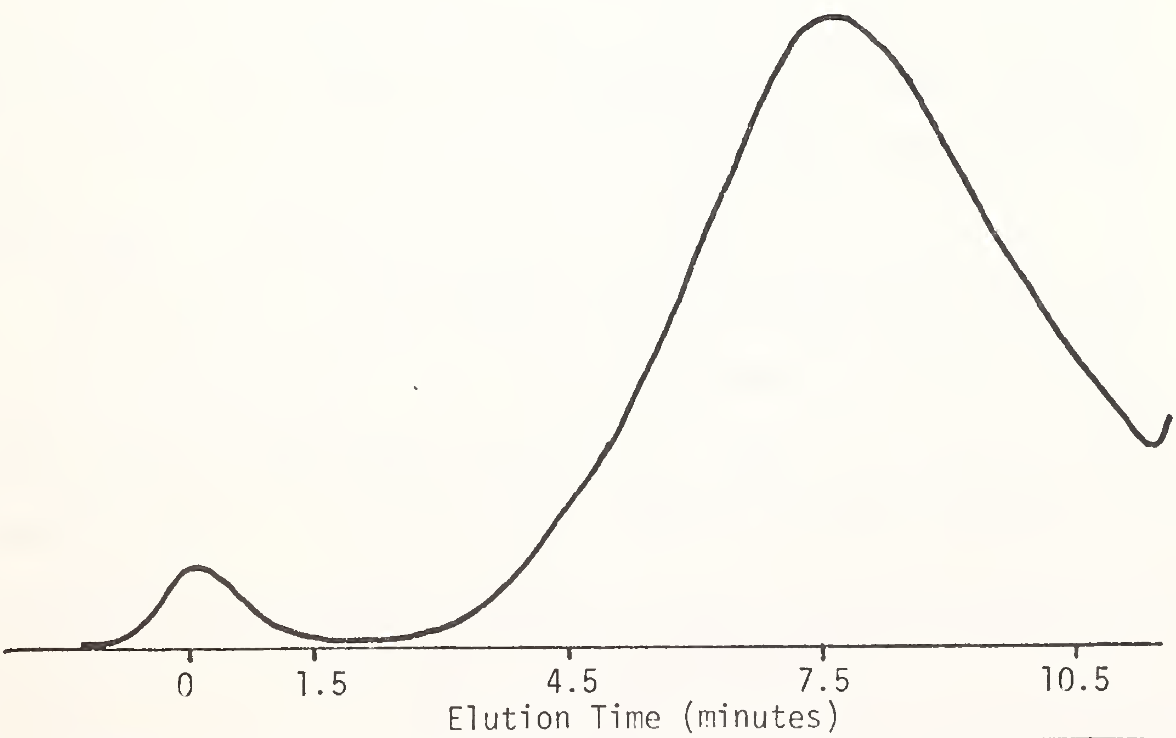

Figure 22B. Chromatographic profile of asphatic oil to produce an excellent pavement.

2. The percentage of molecular size components should be within the following ranges:*

LMS 6-8%

MMS 44-48%

SMS 46-48%

3. The asphaltenes content should range between 12.5 and 16%.

4. The penetration grade should be higher than 120.

VIII. THE 1978 AND 1979 ASPHALTS: DISCUSSION AND APPLICATION OF THE MODEL

The oils (asphalt cements before processing) from the 1978 and 1979 paving season are of interest from several points of view. First, the aquisition of data for these asphalts is important to the assembly of a data bank. Second, the HPLC study of these asphalts can be used to determine the uniformity of asphalts from a given refinery as well as the differences among the products of several refineries. Furthermore, these asphalts may be compared to the model proposed in section VII and some predictions may be made about their long-term performance. These points will be discussed in this section.

The assembly of a data bank on recent asphalts has begun with the 1977 and 1978 roads and has been augmented by a group of 15 asphalts from the 1979 paving season. The latter oils were not accompanied by plant mix or core samples. They are listed in Table 9. The

*Limits were determined by assuming an approximate 2% increase in LMS (relative to the whole asphalt) during processing.

Table 9

Identification	Year	Refiner	% Asphaltenes	% LMS	% MMS	% SMS
85-100 Design Penetration Class						
48.' 15-79 MS 210(2)	1979	D	-	11.4	48.3	40.3
49. 16-79 F 7-1(2)0	"	D	-	-	-	-
39.' Broadway at Helena* M 5816(3)	1978	A	14.4	7.7	52.3	40.0
40.' U. S. #2 Havre-East F1-6 (2)382	"	D	15.3	10.1	51.4	38.5
120-150 Design Penetration Class						
50. 2-79 I 15-5(64)238 U2	1979	D	15.8	-	-	-
51.' 3-79 IR 94-6(32)216	"	B	10.0	5.9	47.7	46.4
52.' 4-79 RS 212-2(2)6	"	A	12.7	8.0	49.4	42.6
53. 5-79 RS-TQS 303-1(3)0	"	A	11.7	-	-	-
54. 6-79 RS TQS 384-1(2)19	"	B	-	-	-	-
55.' 7-79 I 90-9(28)509 U3	"	C	13.1	6.2	47.8	46.0
56.' 8-79 F 83-2(1)65	"	D	14.3	10.6	48.3	41.0
57. 9-79 I 90-5(33)264	"	A	-	-	-	-
58. 10-79 F 93-1(1)0 U2	"	D	-	-	-	-
59. 11-79 F 41-1(4)20	"	B	-	-	-	-
60. 12-79 RS-TQS 384-1(2) 19	"	B	-	-	-	-
61. 14-79 I 90-3(48)176	"	A	-	-	-	-
41.' McDonald Pass-East RF-FF 249(27)	1978	B	13.2	6.4	51.6	42.0
42.' Melville-N & S F 45-1(1)15	"	B	10.4	5.1	46.5	48.5
43.' Sidney-Culbertson-2 F62-1(2)1	"	B	13.4	6.0	49.6	44.4
44.' Two Medicine Bridge-East RF-FLH 353(15)	"	D	14.7	8.0	48.2	43.8
45.' Wolf Point-S.E. F-FLH 25-2(2)47	"	A	13.6	8.5	48.4	43.1
200-300 Design Penetration Class						
62.' 13-79 RS 228-2(4)40	1979	D	-	8.6	51.5	39.8
46.' Big Sandy-Rudyard RS 432-1(2)27	1978	B	8.7	5.8	50.3	43.9
47.' Sidney-Culbertson-1 F 62-1(2)1	"	B	12.1	8.7	49.6	41.6

* This pavement was torn up due to factors unrelated to asphalt and so is included for information only.

' indicates that both Soltec and Data Module spectra are included.

oil samples from 1978 roads are included in this table for ease of comparison.

These asphalts were not treated in any way prior to being dissolved in THF and analyzed by HPLC. Chromatograms of all 1979 samples were obtained by means of the original Soltec recorder; the 1978 and a selected few of the 1979 samples were analyzed also by Data Module. Selected 1979 samples were analyzed for asphaltenes content by the Corbett-Swarbrick method.

The first treatment of the data involved comparisons of the chromatograms of asphalts of different penetration grades from the same refinery. Such comparisons are shown in several figures. In figure 23 are the chromatograms of 3 asphalts from refinery D, whereas 2 oils from refinery A appear in figure 24 and 2 oils from refinery B are given in figure 25. It is readily apparent that there are only minor differences among the asphalts from a single refinery regardless of the penetration grade.

The lack of distinction between pen grades by HPLC may be the result of insensitivity in the HPLC analysis. However, it seems more likely that asphalts of different pen grades from the same refinery really are very much the same. Evidence for this is found in the asphaltenes data and LMS percentages for the asphalts in these figures (Table 10).

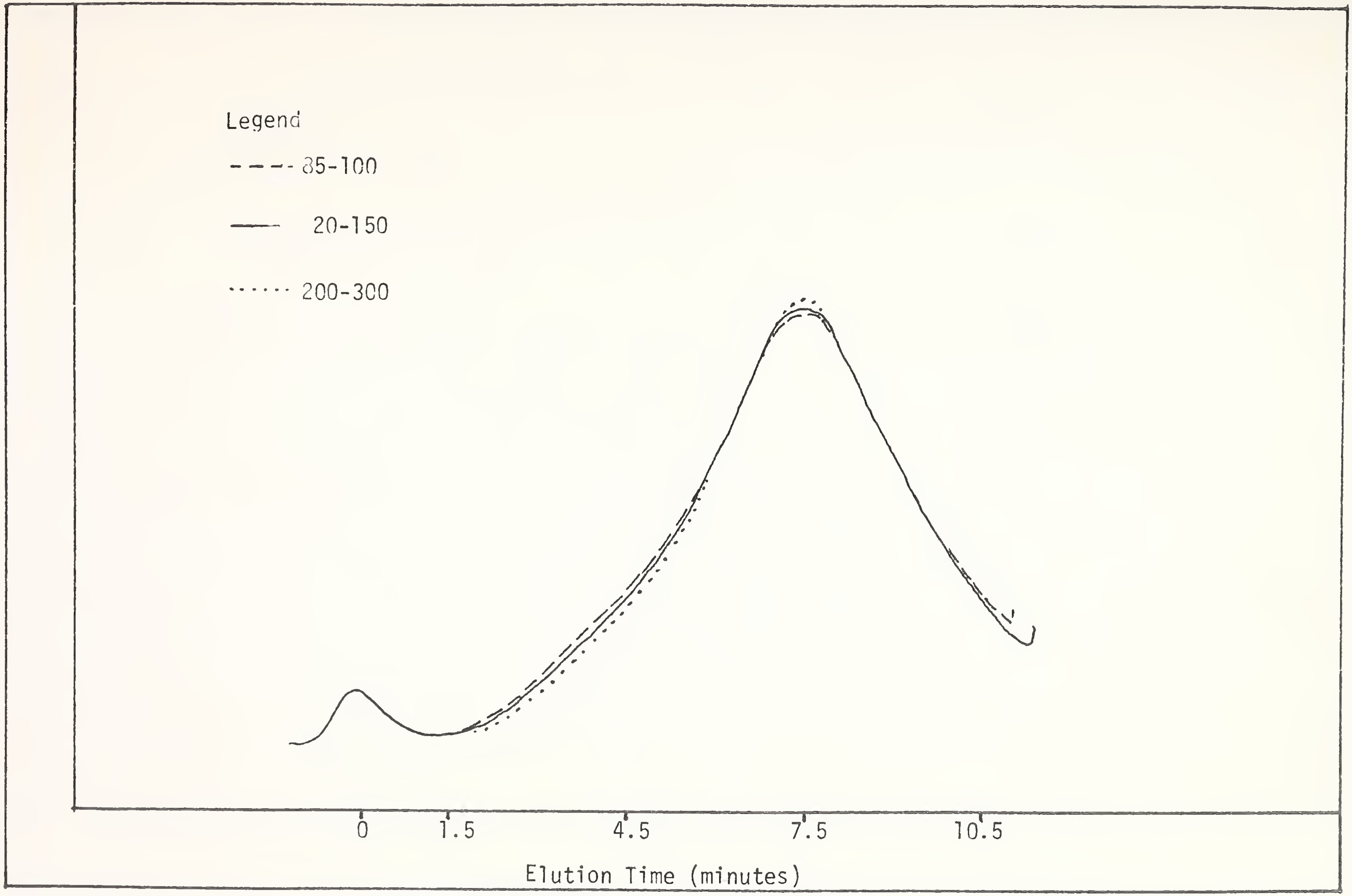

Figure 23. Oils from Refinery D.

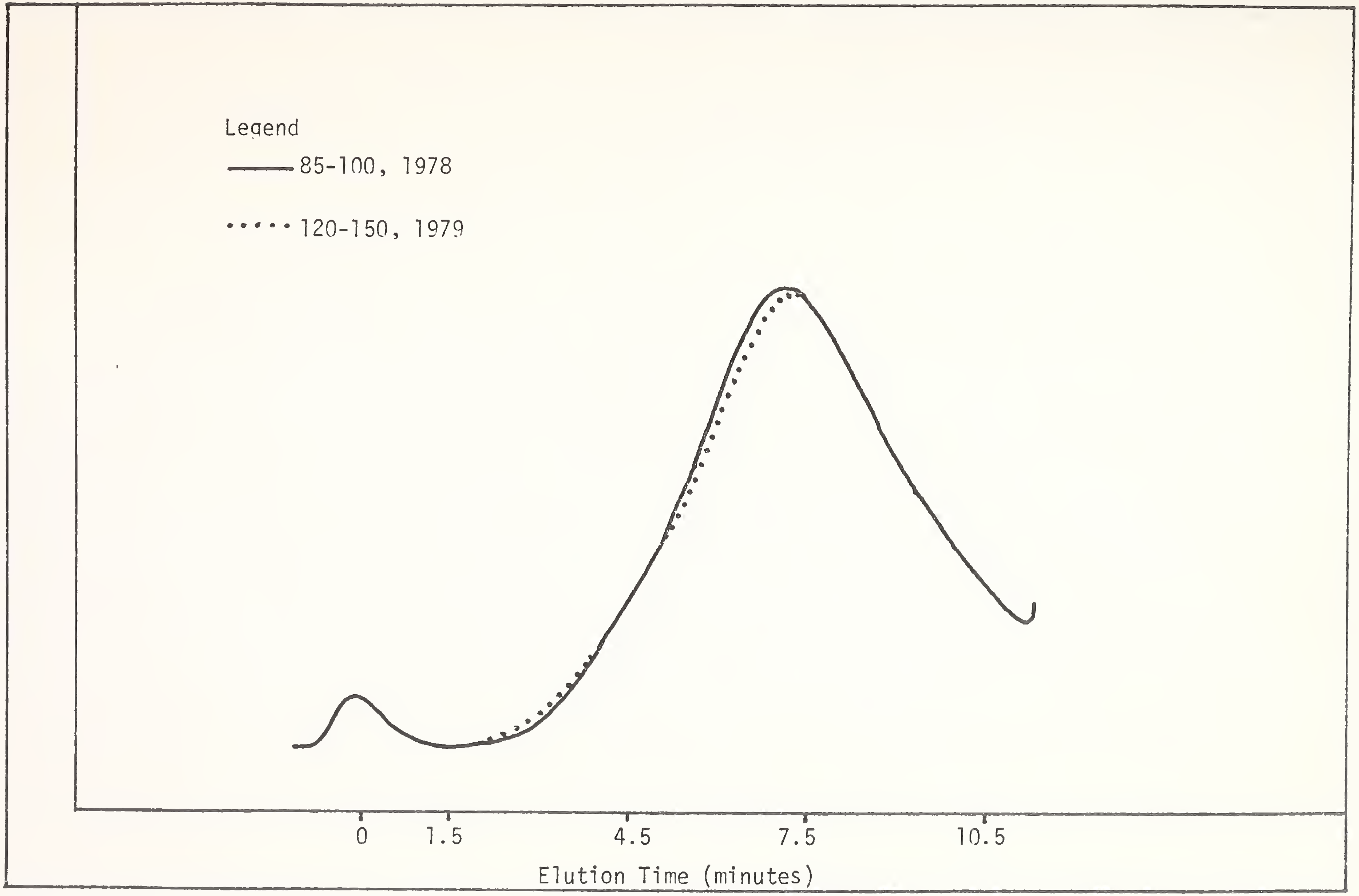

Figure 24. Oils from Refinery A.

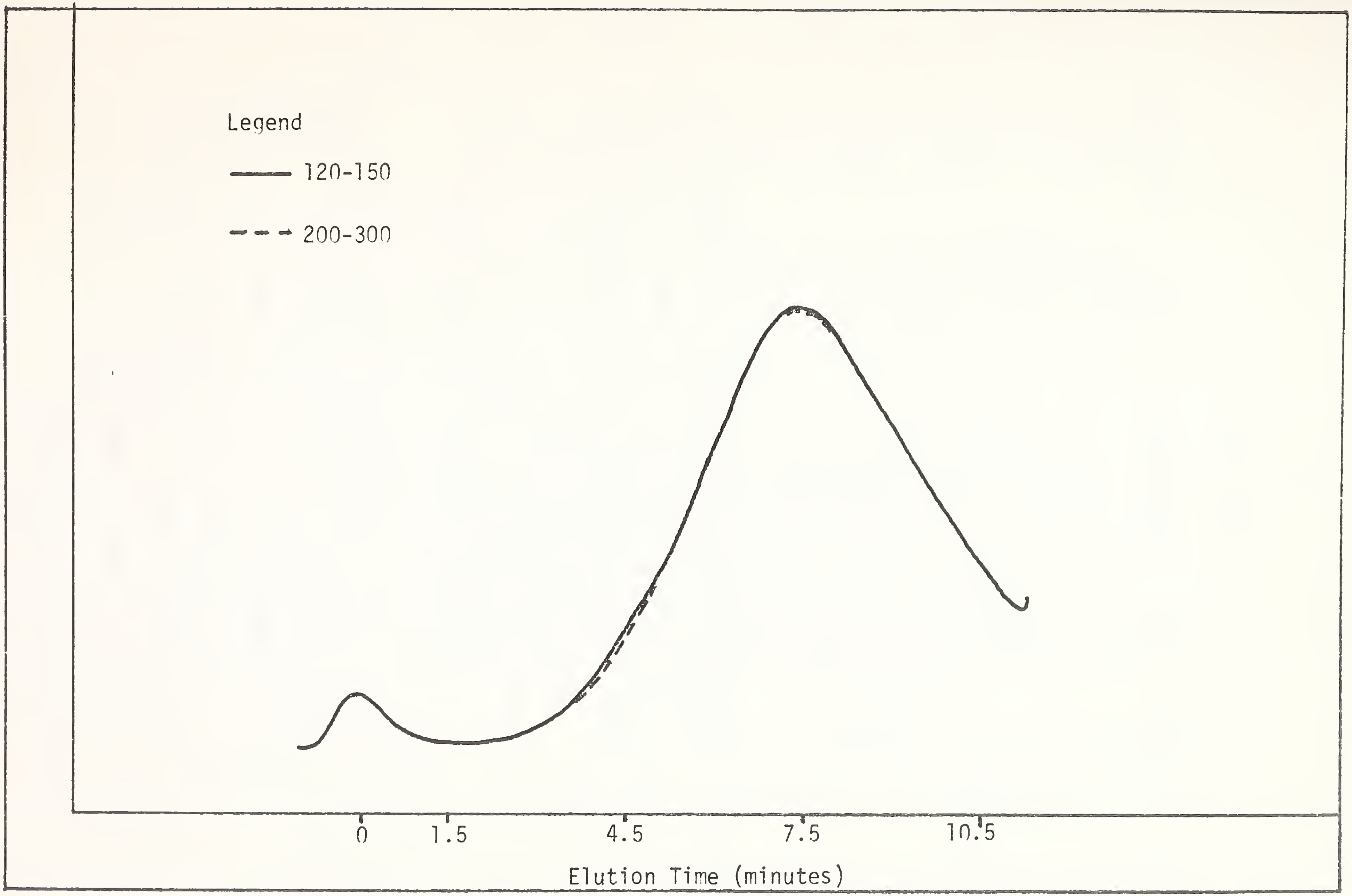

Figure 25. Oils from Refinery B, 1978.

Table 10

Refinery	Pen	% Asphaltenes	% LMS	MMS	SMS
(D)	85-100	-	11.4	48.3	40.3
	120-150	14.3	10.6	48.3	41.0
	200-300	-	8.6	51.5	39.8
(B)	120-150	13.4	6.0	49.6	44.4
	200-300	12.1	5.8	49.6	44.6
(A)	85-100	14.4	7.7	52.3	40.0
	120-150	12.7	8.0	49.4	42.6
(C)	120-150	13.1	6.2	47.8	46.0

For each refinery, it can be seen that the differences in both the LMS area and asphaltenes percentages are relatively small. Furthermore, these changes parallel the small changes visible in the chromatograms. Therefore, the asphalts really are similar. Possibly those components which are added to meet penetration specifications volatilize or polymerize readily and are not detectable.

The data also permits comparison of asphalts of the same penetration grade but from different refineries. Such comparisons are shown in figures 26, 27, and 28. In figures 26 and 27, the differences in the amount and size of LMS components are obvious. With regard to figure 28, several additional points may be made. The greater peak height for the refinery C asphalt causes a little difficulty in such visual tests. However, knowledge of the area per-

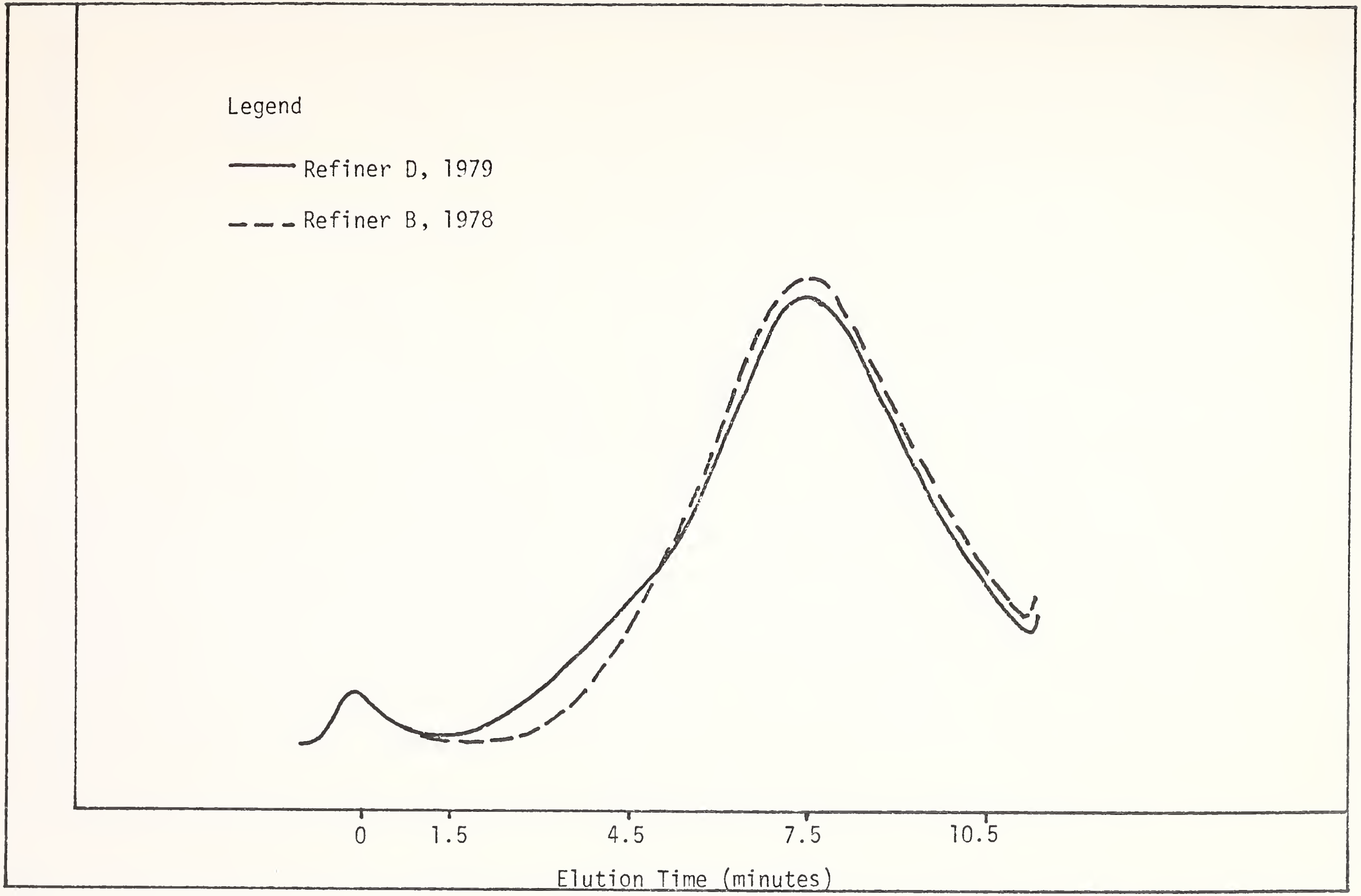

Figure 26. Comparison of 200-300 pen asphalts.

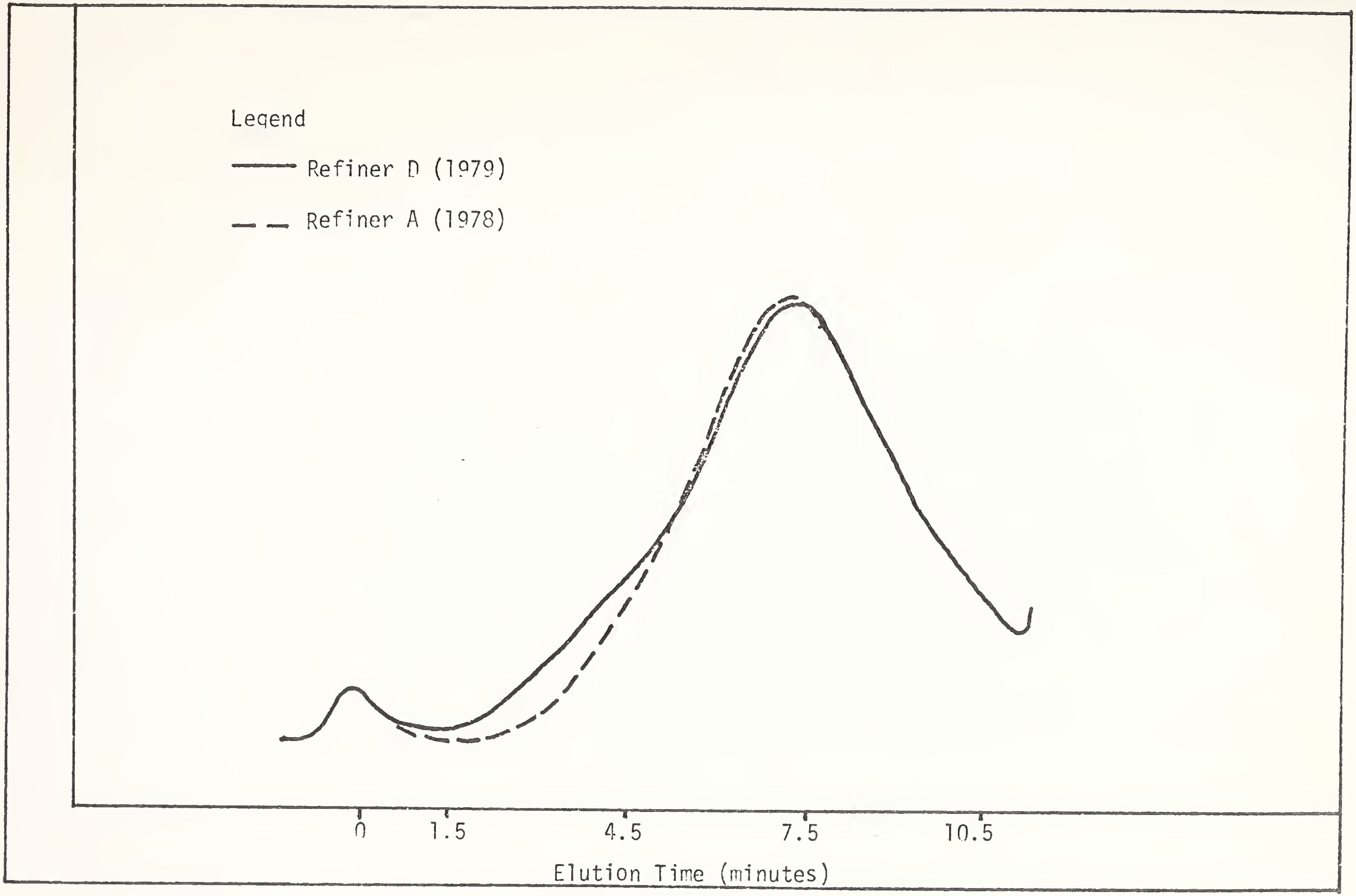

Figure 27. Comparison of 85-100 pen asphalts.

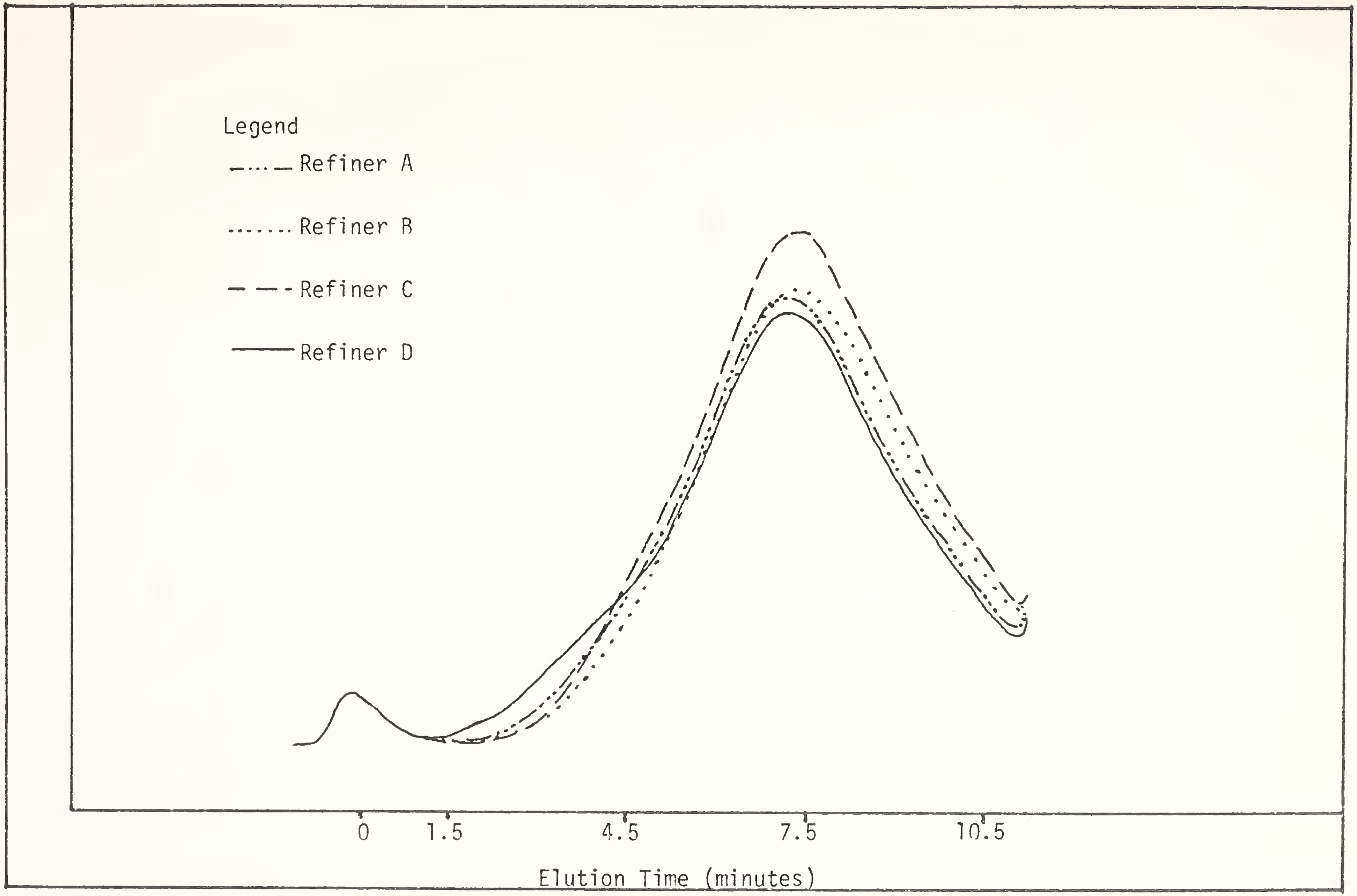

Figure 28. Comparison of 120-150 pen asphalts (1979).

centages from Data Module analysis helps to clarify the situation. These area percentages for figure 28 are condensed in Table 11.

Table 11

Refiner	% Asphaltenes	% LMS	MMS	SMS
A	12.7	8.0	49.4	42.6
B	10.0	5.9	47.7	46.4
C	13.1	6.2	47.8	46.0
D	14.3	10.6	48.3	41.0

From this data, it may be seen that the molecular size compositions of asphalts from refineries B and C are very similar, although C does contain a higher percentage of asphaltenes. Since these two asphalts are essentially alike, we may compare only the asphalts from refineries A, B, and D. It is observed that asphalt from refinery B contains not only the lowest amount of asphaltenes (10.0%) but also the smallest size and amount of LMS components. In fact, its overall molecular size is notably smaller. The asphalt from D, on the other hand, contains the largest amount of asphaltenes (14.3%) and the largest size and amount of LMS materials.

In addition to comparing these new asphalts by penetration grade and by refinery source, it is instructive to compare the 1978 and 1979 oils and 1978 cores with the model of finished high quality asphalt. Figure 29 shows the chromatograms of two 120-150 oils superimposed on that of the model of finished asphalt. Again, differences in LMS and

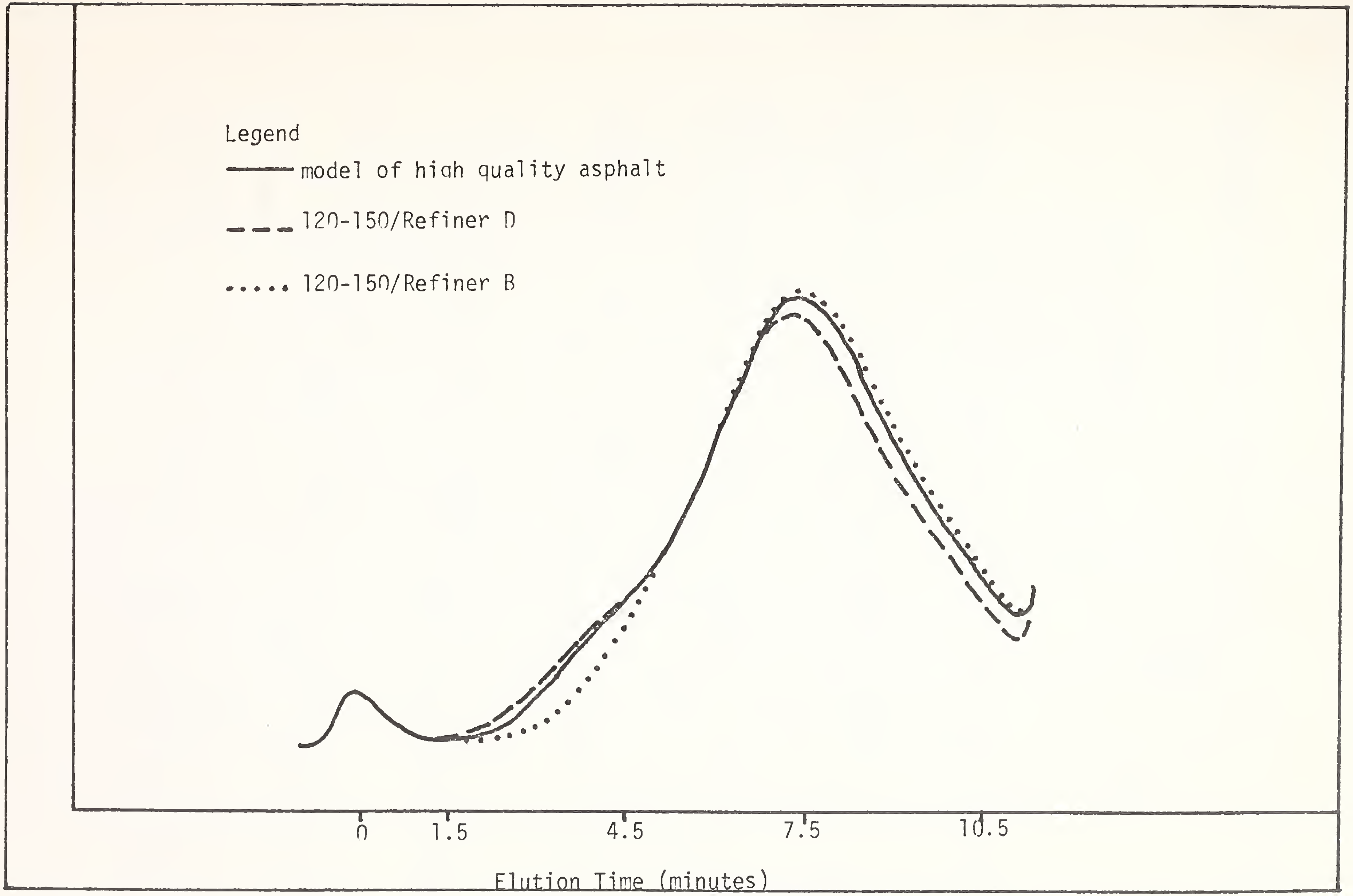

Figure 29. Comparison of 1979 oils with the model

SMS regions are obvious. They are reflected in the area percentages.

	%		
	LMS	MMS	SMS
model (finished)	8.6	45.9	45.5
refiner D (oil)	10.6	48.3	41.0
refiner B (oil)	5.9	47.7	46.4

Mixing in either batch plant or Boeing drum dryer would be expected to increase the disparity between the oil from refinery D and the model in the LMS region but to decrease the disparity between the oil from refinery B and the model. On the basis of size and amount of LMS components and on overall molecular size, the asphalt from D might not be expected to perform as well as the model. It has characteristics similar to established asphalts which have cracked. The asphaltenes percentage is only 14.3, however, which may act as a mitigating factor.

The asphalt from refinery B would not be expected to crack on the basis of LMS and asphaltenes content. However, as stated earlier, no models are available for the performance of asphalt with so small an overall molecular size. It may be that any such "light" asphalt will be especially prone to deformation.

In figure 30, asphalts extracted from cores of two 1978 pavements are compared with the model of finished asphalt. Again there are differences among the curves, especially in the LMS region. Since the 1978 asphalts have been processed by batch plant, no further changes in the LMS region would be anticipated, unless similar changes result from aging.

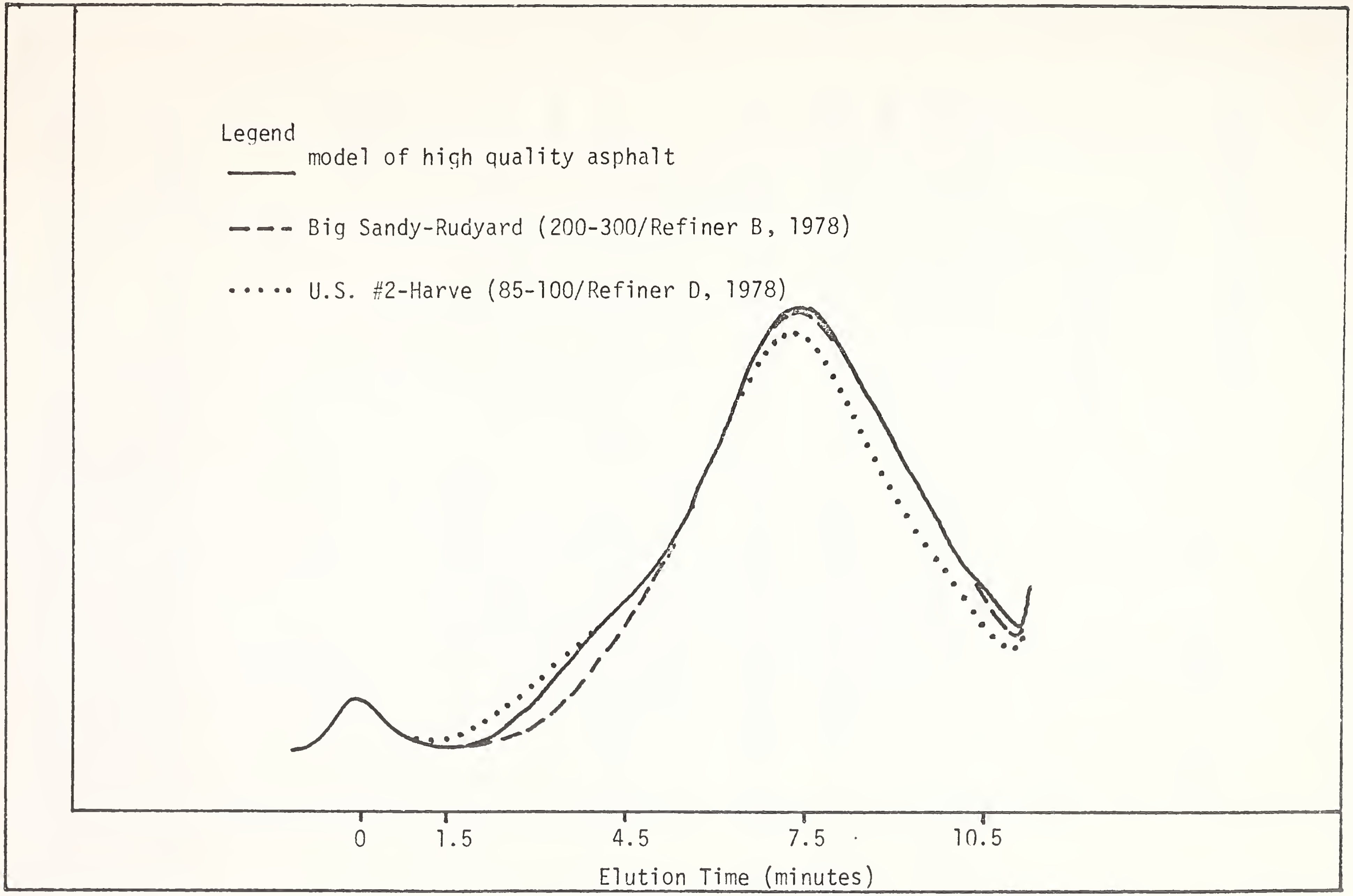

Figure 30. Comparison of asphalts from new cores with the model.

The area percentages are

	% LMS	MMS	SMS
model	8.6	45.9	45.5
Big Sandy-Rudyard	7.5	50.9	41.6
U. S. #2-Havre	12.4	49.7	37.8

The asphalt in U.S. #2-Havre may be expected to crack on the basis the excess size and amount of its LMS component and on its overall molecular size. The asphalt in Big Sandy-Rudyard, on the other hand, would not be expected to crack, but might be subject to deformation.

IX. NEW APPLICATIONS OF THE HPLC TECHNIQUE: THE WIBAUX RECYCLING PROJECT

One section of the Wibaux-E and W road [IR-94-7(15)233 U-1] was selected for recycling by MDH. This road was constructed in 1963 (15 years old at sampling) but had failed. However, failure was attributed to factors others than the asphalt. Analysis showed that the asphalt to be recycled contained 18.3% asphaltenes. HPLC analysis compared with the model of finished asphalt is shown in figure 31. The area percentage analysis is:

	% LMS	MMS	SMS
Wibaux	11.2	46.7	42.1
model	8.6	45.9	45.5

In future recycling projects, HPLC could be used to help ensure the success of the new pavement. Recognizing that there are other factors involved in such cases, the asphalt being recycled could be mixed with new

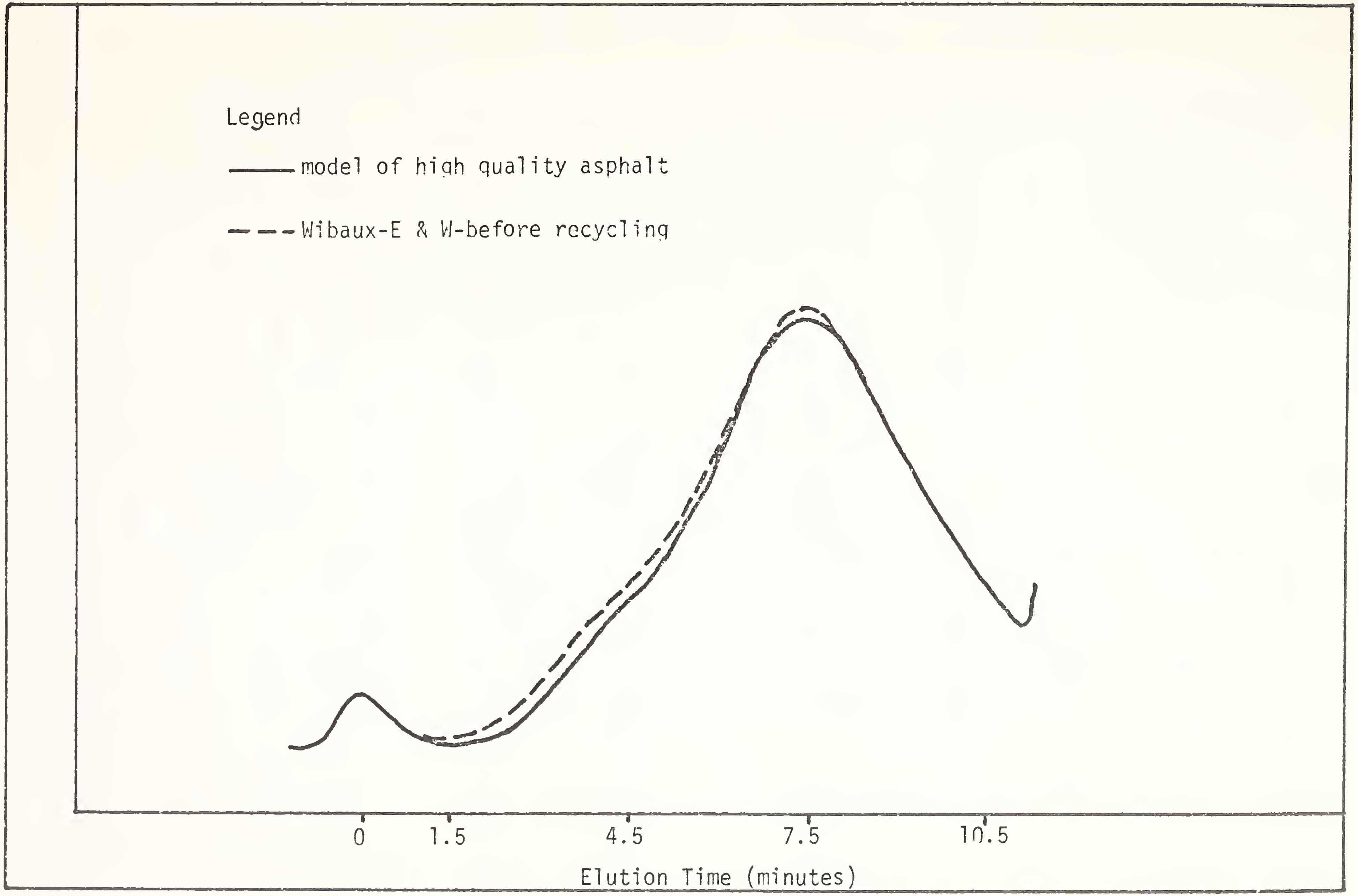

Figure 31. The Wibaux recycling project.

asphalt. Knowing the asphaltenes percentage and the area analysis from HPLC of both the recycled and new asphalts would permit an optimum mixture to be determined. For example, if a new asphalt with the following area and asphaltenes analysis were used:

		%	
asphaltenes	LMS	MMS	SMS
10.4	5.1	46.4	48.5

a 1:1 mixture with the Wibaux asphalt would analyze:

14.3	8.1	46.6	45.3

These values are very similar to those for the model and, therefore, should indicate an acceptable asphalt. Of course, neither asphalt should show any unusual molecular size characteristics.

X. CONCLUSIONS

In this study, the findings of the first project have been elaborated and refined. A system of analysis using gel permeation columns for high performance liquid chromatography (HPLC) has been described. Better methods for preparation of asphalt samples for HPLC have been defined.

The HPLC analysis provides a visual representation of the molecular size distribution in an asphalt. When a Data Module is connected, a mathematical statement of the relative amount of a given molecular size component is available.

The HPLC technique is useful for a variety of purposes.

1. HPLC and asphaltenes analysis have been used to define the characteristics of an asphalt which has shown satisfactory

durability and longevity. Asphalts which closely match these characteristics (page 57) should meet the performance requirements of the Montana Department of Highways.

2. HPLC has been used to characterize the asphalts from each of the four Montana refineries.

3. Using HPLC, the large molecular size (LMS) portion of asphalt was shown to be composed of other constituents in addition to asphaltenes. Furthermore, measurement of asphaltenes content alone does not provide sufficient data on which to judge the quality of an asphalt.

4. Processing through either a batch or drum dryer plant was shown by HPLC analysis to cause a 20 to 80 percent increase in LMS components.

5. Although only one direct comparison was available for the effects of lime on asphalt, it was concluded that a substantial increase in the LMS components can be engineered by the use of lime.

6. It is suggested that the HPLC technique will be useful in additional cases, particularly in recycling asphaltic pavements.

APPENDIX

A. EXTRACTION OF CORES OR PLANT MIX

Asphalt was removed from roadway cores and from plant mix by a reflux procedure. The top 1/2 inch of each core was removed and the sample placed in a 115 x 310 mm cellulose extraction thimble (Schleicher and Schull). The thimble was placed in a wire basket and suspended in a glass extraction flask (approx 14 x 52.5 mm) topped with a large condensing column. The wires from the basket were run through the condenser to provide a means of lifting the thimble above the solvent level. Benzene (Baker, reagent grade) was then added to a level below the top of the thimble. The system was refluxed for 4-8 hours. The thimble was then raised above the solvent level and refluxing was continued (8 hours to overnight). The extraction was complete when the aggregate looked clean on visual inspection and the solvent passing through the thimble was straw colored. This procedure is a modification of AASHTO designation: T 164-76.

B. REMOVAL OF SOLVENT FROM EXTRACTED ASPHALT: PREPARATION FOR PENETRATION AND DUCTILITY TESTING

Solvent was removed from the asphalt which has been extracted from cores or plant mix by first concentrating the solution at 25°C and aspirator pressure in a rotovap (Büchi). When no further solvent could be removed, the asphalt was transferred to a smaller flask and rotovapped at 128-132°C and reduced pressure of 25mm Hg for 20 minutes. The hot asphalt was then transferred to 3 oz. cans for

physical testing and storage.

C. SEPARATION OF ASPHALTENES FROM ASPHALT

One gram of asphalt prepared as described above was refluxed with 100 ml heptane (reagent grade) for 3 hours, then filtered through a GFA glass filter using a Millipore unit. The insoluble material plus the filter were again refluxed for 30 min. in 50 ml fresh heptane. The solid portion constituted the asphaltenes fraction. It was dissolved in tetrahydrofuran (THF, UV-grade, Burdick and Jackson), then rotovapped as above and weighed. The heptane-soluble materials were also rotovapped and weighed. The percentage of asphaltenes in the sample was then calculated.

D. ANALYSIS OF ASPHALT BY HPLC

The high performance liquid chromatography instrument (Waters Associates) consisted of a high pressure pump (M 6000 A), an injector, (Model U6K), a detector (Model R401 differential refractometer) and 5 μ-styragel columns arranged in the order: one 10^3 Å, three 500 Å, one 10^5 Å and one 100 Å. UV-grade THF was used as eluent.

A 1% solution of polystyrene standard (MW = 35,000) in THF was prepared. This solution was used in the preparation of 2% solutions of asphalt. The asphalt was either prepared as above or taken directly from the can of untreated asphalt supplied by MDH.

The instrument was operated in accordance with manufacturer's instructions. When using a Soltec strip chart recorder, 1 ml of sample was injected at a pumping rate of 3 ml/min and a chart speed of 3 cm/min.

When using the Data Module (Waters) as a recorder, 1 ml of sample was injected but the pumping rate was reduced to 2 ml/min and the chart speed to 1 cm/min. The Data Module was programmed to find the area of successive slices 0.3 min wide. (See page 37). The percentage of the total area in each of three 3-minute segments of the curve was calculated separately.

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Rostler, F. G. and R. M. White, Proc. Assoc. Asphalt Pav. Technol. 31, 35 1962.

Jennings, P. W., et. al., Chemical Composition of Commerical Asphalt Cement as Determined by High Pressure Liquid Chromatography, Report No. FHWA-MT-7927, 1977.

Implementation

The results garnered from this and the previous project show conclusively that HPLC analysis of asphalt provides data which is essential to asphalt quality control. Therefore, the following recommendations are forwarded to the Montant Department of Highways.

1. The steps necessary to begin the process which will incorporate the findings of the work into an asphalt specification should now be taken.
2. HPLC analyses should be used in the process of designing the pavement in order to maximize the agreement of the asphalt with the model.
3. The use of HPLC to determine the effects of aggregate, fillers and additives should be actively pursued.
4. A computer bank or log of information about current asphalts and the corresponding roadways should be established and maintained.
5. Roadway performance should be monitored every 2 years for the above data bank.
6. HPLC should be used in the design of recycling projects.